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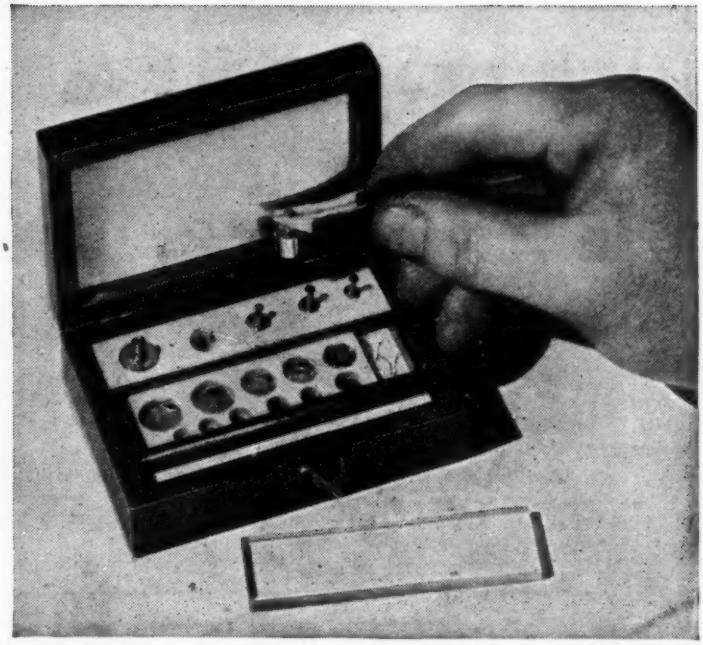

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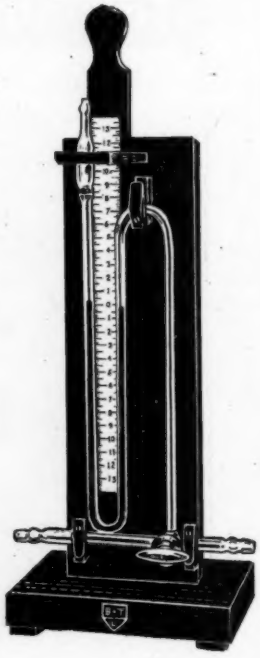

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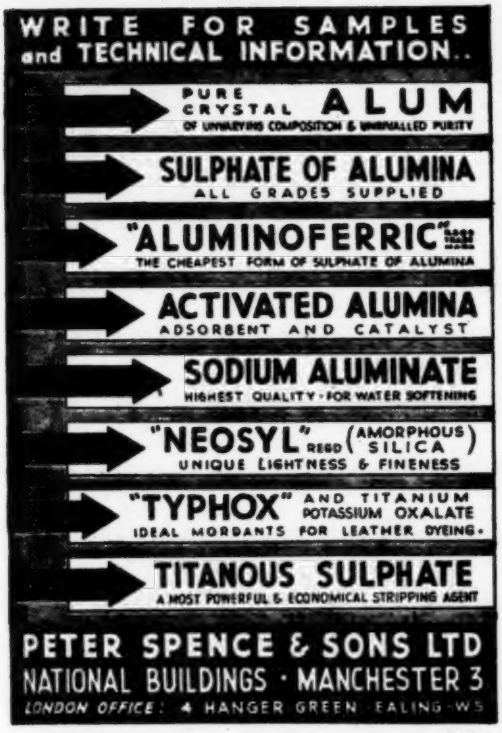
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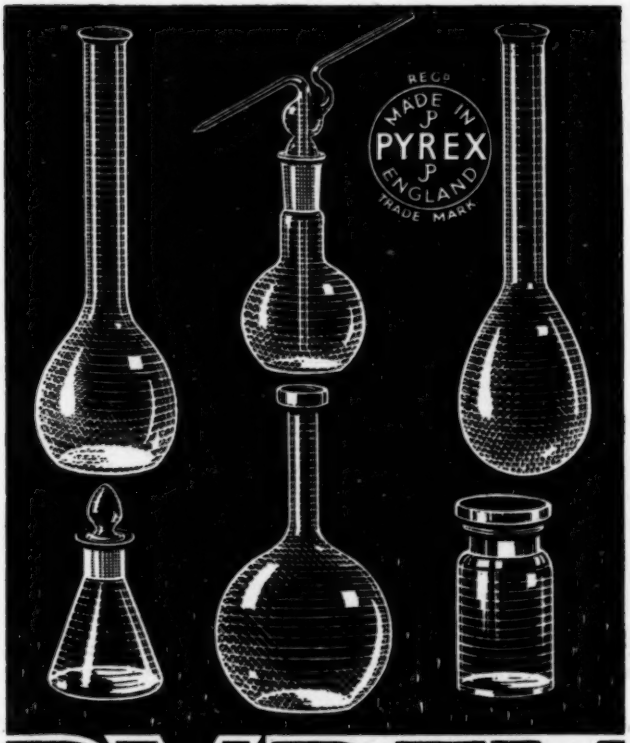

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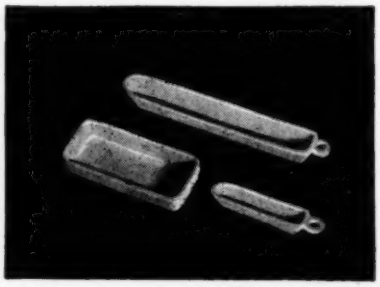

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alcoholic solution was at 4750 A. The dye sensitised a gelatinochloride photographic emulsion moderately well, with the maximum effect at 4950 A.

Bis-2-(3-*methyldihydro*-1 : 3-*thiazine*)*trimethincyanine Iodide* (XIII; R = Me).—2-Methyldihydro-1 : 3-thiazine methiodide (3 g.; 2 mols.), ethyl orthoformate (9 c.c.; 4 mols.), and pyridine (25 c.c.) were refluxed for 1½ hours. Ether precipitated a tar from the orange reaction mixture and this changed to a red solid (0·56 g.) on treatment with water. After recrystallisation from absolute alcohol (11 c.c.), the yield was 13% (Found: I, 31·9. $C_{19}H_{21}N_2IS_2$ requires I, 32·0%). The deep red crystals had m. p. 188° (decomp.). The methyl-alcoholic solution showed a narrow absorption band with maximum at 4600 A. Towards a washed chloride emulsion the dye is a weak sensitiser with maximum about 4850; sensitisation extends from 4400 to 5200 A.

Bis-2-(3-*ethyldihydro*-1 : 3-*thiazine*)*trimethincyanine Iodide* (XIII; R = Et).—This was prepared from the ethiodide, heating being prolonged for 3 hours. The precipitated dye was recrystallised from absolute alcohol (30 c.c. per g.) and thus obtained in 16% yield (Found: I, 30·0. $C_{19}H_{25}N_2IS_2$ requires I, 29·9%). The deep red crystals had m. p. 243° (decomp.) and their methyl-alcoholic solution had an absorption maximum at 4600 A. A chloride emulsion was strongly sensitised from 4400 to beyond 5200 with a maximum at about 4850 A. This dye has been described as melting at 248—249° (decomp.) and showing a sensitising maximum of 5000 A. in a bromide emulsion (F.P. 850,653/1939).

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)] [2-(3-*ethylbenzoxazole*)]*trimethincyanine Iodide* (XV; Y = O).—2-Methyldihydro-1 : 3-thiazine methiodide (2·57 g.; 1 mol.), 2-β-acetanilidovinylbenzoxazole ethiodide (4·34 g.; 1 mol.), triethylamine (2 c.c.; 1·5 mols.), and absolute alcohol (20 c.c.) were boiled together, with stirring, for 5 minutes. The product was washed with water and with ether (0·9 g. obtained) and, after recrystallisation from methyl alcohol (30 c.c.), resulted in 19% yield (0·8 g.) (Found: I, 29·5. $C_{17}H_{21}ON_2IS$ requires I, 29·6%). The bright reddish-orange crystals had m. p. 270° (decomp.). The methyl-alcoholic solution had a well-defined absorption band with its maximum at 4700 A. and an inflection at 4500. It is a good sensitiser for a chloride emulsion, the maximum effect being at 5050 A.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)] [2-(3-*ethylbenzthiazole*)]*trimethincyanine Iodide* (XV; Y = S). This was prepared from 2-methyldihydro-1 : 3-thiazine methiodide, 2-β-acetanilidovinylbenzthiazole ethiodide, and triethylamine in alcohol. The washed product was first boiled out with methyl alcohol, and the residue then recrystallised from it (13 c.c. and 39 c.c. per g. taken), being obtained in 13% yield (Found: I, 28·4. $C_{17}H_{21}N_2IS_2$ requires I, 28·6%). The red crystals had m. p. 275° (decomp.). The absorption maximum was at 5050 A. and the sensitising maximum, which was conferred on a bromide emulsion, was at 5400 A. A gradual fall of sensitivity in the region 5700—6100 A., however, indicated the presence of impurity, doubtless the symmetrical thiacarbocyanine, which is an exceptionally good sensitiser. An alternative method of preparation from 2-methylbenzthiazole ethiodide, 2-β-acetanilidovinyldihydro-1 : 3-thiazine methiodide, and triethylamine in alcohol likewise gave a product which, although analytically pure, was shown by the far more delicate photographic test to contain the trace of impurity.

5 : 2′-(3′-*Ethyltetrahydro*-1′ : 3′-*thiazyl*)-3-*ethylrhodanine* (XVIII).—2-Ethylthiodihydro-1 : 3-thiazine ethiodide (1·59 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), triethylamine (2 c.c.; 1·5 mols.), and absolute alcohol (7 c.c.) were boiled together, with stirring, for 3 minutes. The water-washed product was crystallised from absolute alcohol (4·5 c.c.), after which the yield was 60% (0·87 g.). After recrystallisation from light petroleum (b. p. 80—100°) (100 c.c. per g.), the yield of bright yellow crystals, m. p. 102°, was 44% (Found after drying in a vacuum desiccator: S, 33·6. $C_{11}H_{16}ON_2S_3$ requires S, 33·4%). The absorption maximum of the methyl-alcoholic solution is at 4120 A. The substance is a good sensitiser for a washed chloride emulsion, having a maximum at 4400 and extending the sensitivity to 4800 A.

5 : 2′-(3′-*Methyltetrahydro*-1′ : 3′-*thiazyl*)*ethylidene*-3-*ethylrhodanine* (XIX).—2-β-Acetanilidovinyldihydro-1 : 3-thiazine methiodide (XV; R = Me) (1·52 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), triethylamine (0·7 c.c.; 1·1 mols.), and absolute alcohol (15 c.c.) were boiled and stirred together for 4 minutes. The product was washed with ether (0·55 g. obtained) and recrystallised from pyridine (5 c.c.), after which the yield was 13% (Found: S, 32·2. $C_{13}H_{16}ON_2S_3$ requires S, 32·0%). The dull red solid had m. p. 195° (decomp.). Its methyl-alcoholic solution had its absorption maximum at 4950 A. and an inflection at 4700. The compound sensitised an iodobromide emulsion moderately up to 5800, with a maximum at 5450 A., but reduced the original blue-sensitivity,.

5 : 2′-(3′-*Methyltetrahydrothiazolyl*)*ethylidene*-3-*ethylrhodanine*.—2-β-Anilinovinylthiazoline methiodide (1·79 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), triethylamine (1·0 c.c.; 1·5 mols.), and absolute alcohol (10 c.c.) were boiled and stirred together for 10 minutes. The product was washed with ether and with water (0·88 g. obtained) and recrystallised from acetic acid (25 c.c.), after which the yield was 52% (Found: S, 33·6. $C_{11}H_{14}ON_2S_3$ requires S, 33·6%). M. p. 219° (decomp.). A methyl-alcoholic solution of the orange-red crystals had its absorption maximum at 4840 A. The preparation of this dye and its sensitising action have been described in the patent literature (Kodak Ltd., B.P. 450,958/1934, ex. 48).

We are indebted to several colleagues for help: to Dr. E. P. Davey for testing the sensitising action of the compounds, to Miss M. D. Gauntlett and Mr. R. B. Morris for plotting absorption curves in the ultra-violet and visible regions, to Mr. E. D. Rowell for photographs of absorption spectra in the visible region, and especially to Dr. L. G. S. Brooker for his constructive criticism.

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[*Received, April 12th*, 1943.]

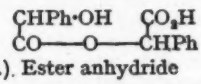
NOTE.

The Effect of Heat on Mandelic Acid. By W. ROGIE ANGUS and R. P. OWEN.

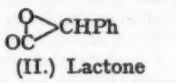
IT has been observed that the m. p.'s and f. p.'s of *l*-mandelic acid are progressively and considerably lowered after each successive heating, and in order to ensure that this was not due to racemisation or incomplete resolution, *r*-mandelic acid has been similarly studied and found to exhibit the same behaviour. Since this work is only incidental to that reported in this vol., p. 227, however, it has not been pursued beyond the stage now reported, which has established that mandelic acid undergoes some change in structure and composition on being melted, and proved that the f. p. curve of mixtures of *r*- and *l*-mandelic acids cannot be determined by the usual methods. The lowering of the m. p. is reproducible and appears to be a function of the temperature and time of heating. When mandelic acid is esterified or acylated, this behaviour is not encountered, indicating that the phenomenon is due to some reaction involving either or both the hydroxyl and the carboxyl group, probably internal ester formation. The property of forming internal esters on heating is characteristic of α-hydroxy-acids, *e.g.*, lactic acid, and it is conceivable, therefore, that the behaviour of liquid (fused) mandelic acid will be analogous. Kishner (*J. Russ. Phys. Chem. Soc.*, 1925, **56**, 15) reported that when *r*-mandelic acid is heated alone to 130°, or in a sealed tube with water, the m. p. is lowered from 118° to 105—106°.

The first fusion gave a m. p. of 118° and a f. p. of 114·4°, the maximum temperature attained by the fused acid being 120°. The second fusion gave an arrest in the cooling curve at 112—114·8°, and after heating to 125° the subsequent cooling curve showed a f. p. of 108·4°. After further heating to 133°, the cooling curve showed the new f. p. to be 102·2°. The acid was kept at 133° for 30 mins., and the resulting compound showed no definite f. p. but passed gradually into a semi-solid state on cooling. When *r*-mandelic acid (m. p. 118°) was kept in a sealed glass tube at 120° ± 1° for 6 days it became a yellow oil, cooling to a thick syrup which, with 2 : 4-dinitrophenylhydrazine, gave no indication of the presence of an aldehyde. Sodium carbonate completely removed the syrup from an ethereal solution, and on standing yielded a white precipitate (insoluble in hydrochloric acid) which, after two recrystallisations from alcohol and one from benzene, had m. p. 136°. As water seemed to be given off during the heating, the experiment was repeated except that the tube containing the mandelic acid was fitted with side tubes containing phosphoric anhydride. Water distilled into these side tubes. After being heated for 7 days, the resulting oil, on cooling, solidified into a transparent glass (m. p. 73—75°); this was easily soluble in acetone, chloroform, and alcohol, but only slightly soluble in ether, from which it could be extracted by cold sodium carbonate solution. On standing, the extract deposited a white, semi-liquid mass. The supernatant liquid was decanted, and the semi-liquid shaken with alcohol; a white precipitate was obtained which had no definite m. p. and was the sodium salt of some acid. Hydrolysis with hydrochloric acid gave a white precipitate, which, after repeated recrystallisation from alcohol, had m. p. 130°. Analysis of the glassy material obtained on heating gave C, 64·7, 64·5, 64·6; H, 4·6, 4·7, 4·8%, but no acceptable empirical formula can be derived from these results.

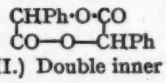
Bischoff and Walden (*Annalen*, 1894, **279**, 118) found that when mandelic acid was heated to 200—205°, water and benzaldehyde were given off and a glassy material (m. p. 60°) remained; this showed no reaction with sodium carbonate solution, and, from analysis, appeared to be a mixture of (I), (II), and (III). By comparing the analytical data now



(I.) Ester anhydride



(II.) Lactone



(III.) Double inner anhydride

obtained with those of Bischoff and Walden and with the values calculated for these condensation products, it becomes evident that the present results cannot be reconciled with their interpretation.

	C, %.	H, %.
Present results	64·6	4·7
B. & W.	69·7	4·8
Ester anhydride (I)	67·1	4·9
Lactone (II) and inner anhydride (III)	71·6	4·5

The conditions of heating in the two investigations were widely different and, although the condensation products would appear to be almost certainly a mixture, the low value for carbon now obtained casts doubt on the possibility of (I), (II), or (III) having been formed under the present experimental conditions. It would appear, therefore, that the extent to which condensation occurs and the products of condensation are governed by the temperature to which the acid is heated and by the method of heating.—UNIVERSITY COLLEGE OF N. WALES, BANGOR. [*Received, January 5th*, 1943.]

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64. *The Structure of the Boron Hydrides.*

By H. C. LONGUET-HIGGINS and R. P. BELL.

It is suggested that the hydrides of boron contain the hydrogen bridge linkage $>B<\begin{smallmatrix}H\\H\end{smallmatrix}>B<$, which can be formulated as a resonance hybrid between structures containing only normal electron-pair bonds. It is shown that this type of linkage is intrinsically no less probable than the accepted resonance structure containing one-electron bonds, and that boron and gallium are the only elements known to form covalent hydrides which would be expected to contain such a linkage. The borohydrides of beryllium and aluminium are naturally accounted for by the same hypothesis. The experimental data for the electron diffraction, Raman spectrum, infra-red spectrum, and specific heat of diborane are analysed and shown to support a bridge configuration rather than one resembling ethane. Structures are suggested for the higher boron hydrides.

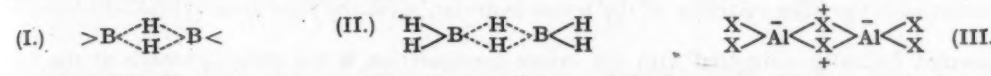
THE molecular formulæ of the hydrides of boron cannot be accounted for in terms of normal electron-pair links, since the total number of electrons present in the outer shells is not sufficient for this purpose. A formulation containing purely ionic links is at variance with the properties of the substances concerned, and it is therefore necessary to postulate some abnormal type of linkage. A number of structures involving one-electron links have been proposed, and the current view is that the boron hydrides can be represented as resonance structures in which each bond is a hybrid between a two-electron link, a one-electron link, and a state in which there is no linkage; for instance, diborane, B_2H_6, is supposed to have the same configuration as ethane, every link in the molecule having this hybrid character. The interpretation of the chemical and physical properties of the boron hybrides in terms of this type of structure has been summarised in two recent reviews (Schlesinger and Burg, *Chem. Reviews*, 1942, **31**, 1; Bauer, *ibid.*, p. 43).

There are, however, a number of difficulties connected with this hypothesis. The one-electron link is not met with elsewhere in chemistry except in the transient species H_2^+, which, having only one electron, has no alternative. This species can thus hardly be compared with diborane, where the "abnormal" molecule B_2H_6 appears to be more stable than the "normal" (but hypothetical) system $2BH_3$, in which all the electrons are paired. The diamagnetic character of diborane and the fact that every known hydride of boron contains an even number of valency electrons do not follow naturally from the assumption of one-electron links, and suggest rather some structure in which all the electrons are paired. Moreover, it has proved very difficult to account for the observed Raman and infra-red spectra of diborane on the basis of a configuration resembling ethane.

It is the purpose of the present paper to show that another type of resonance linking is intrinsically no less

probable than the usually accepted one, and that it leads to a configuration in better harmony with the experimental facts. We shall deal mainly with the physical evidence, since most of the chemical facts can be explained equally well on either hypothesis. Adequate physical data are available only for diborane, but the problem of the higher hydrides of boron will also be treated briefly.

The Bridge Structure.—The type of structure which we advocate contains linkages which may be written as in (I), there being no direct link between the two boron atoms. Diborane, for example, is written as (II),



where the terminal B–H bonds are normal two-electron links, and the four valencies are arranged tetrahedrally about each boron atom. This structure bears a close resemblance to the accepted one for the dimeric aluminium halides, *viz.*, (III) (where X is a halogen), but differs essentially from that of ethane. It was first proposed by Dilthey (*Z. angew. Chem.*, 1921, **34**, 596; cf. also Core, *Chem. and Ind.*, 1927, **5**, 642), who did not, however, make any suggestion as to the nature of the bridge linkages. More recently, it has been pointed out that the bridge linkage can be formulated as a resonance hybrid between either of the following pairs of equivalent structures, (IV*a*) and (IV*b*). Resonance between the covalent structures (IV*a*) has been suggested by Nekrassov

(*J. Gen. Chem. Russia*, 1940, **10**, 1021, 1156), and the ionic structures (IV*b*) are favoured by Syrkin and Diatkina (*Acta Physicochim. U.R.S.S.*, 1941, **14**, 547), but no thorough discussion has been given of the theoretical implications or practical consequences of these formulæ.

Since all the resonance forms suggested contain only paired electrons, the bridge linkage provides a ready explanation of the diamagnetic character of diborane, and of the fact that every known hydride of boron contains an even number of electrons. The absence of a direct link between the boron atoms accounts for the ease with which the various hydrides are interconverted, and the facility of reactions like $B_2H_6 + 2CO \longrightarrow 2\bar{B}H_3\cdot\overset{+}{C}O$, $B_2H_6 + 2NMe_3 \longrightarrow 2\bar{B}H_3\cdot\overset{+}{N}Me_3$, $B_2H_6 + 2NH_3 \longrightarrow \overset{+}{N}H_4[\bar{B}H_3\cdot\overset{+}{N}H_2\cdot\bar{B}H_3]$, etc. It is also significant that mono-, di-, tri-, and tetra-methyldiborane are all known, but that attempts to prepare the penta- and hexa-methyl compound have failed; moreover, hydrolysis shows that neither the tri- nor the tetramethyl compound has more than two methyl groups attached to the same boron atom. The one-electron link hypothesis provides no reason for this behaviour, but it is explained by the bridge structure, which requires at least one hydrogen on each boron atom. Similarly, trimethyboron is known, but not the di- or the monomethyl derivative, which presumably dimerise through their hydrogen atoms to give tetra- and di-methyldiborane, respectively.

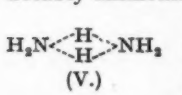
The Nature and Occurrence of the Resonance Link.—The linking of two boron atoms through a bridge of two apparently bivalent hydrogen atoms can be formally described as a pair of "hydrogen bonds," but it differs essentially from the linkage which occurs, *e.g.*, in the association of compounds containing hydroxyl or imino-groups. The latter classes of hydrogen bonds were at one time attributed to resonance of the type {X–H Y, X H–Y} (see, *e.g.*, Sidgwick, *Ann. Reports*, 1933, **30**, 112) but are now believed to depend on electrostatic attraction between a dipole $\overset{\leftarrow\!+}{X\text{–}H}$ and an unshared pair of electrons on the atom Y (cf. Pauling, "The Nature of the Chemical Bond," Chap. 9, 1940). This kind of linkage is very unlikely to occur in the boron hydrides, since the link >B–H will have a much smaller dipole moment than –OH or >NH, and there are no unshared electrons on the (hypothetical) molecule BH_3. We shall therefore use the term "resonance link" for the bridge linkage in the boron hydrides, in order to distinguish it from the more usual type of hydrogen bond.

There is a considerable amount of both theoretical and experimental evidence that resonance between equivalent bond assignments can contribute greatly to the stability of a system, though it is not usually considered that two parts of a molecule can be held together solely by such resonance stabilisation. Thus, from the fact that the reaction $H + H_2$ (para-hydrogen $\longrightarrow$ ortho-hydrogen) has an activation energy of only about 9 kg.-cals./mole, we can conclude that the lowest energy for the symmetrical configuration H···H···H is 90 kg.-cals./mole lower than that of three hydrogen atoms, though it is still slightly higher than that of the system $H + H_2$, and therefore constitutes an activated state rather than a stable molecule. The formation of a stable molecule by resonance will be opposed by the energy needed to stretch the links of the constituent parts and to bring these parts close together, but there is no theoretical reason why this expenditure of energy should always exceed the resonance stabilisation. Theoretical calculations of the energy are subject to many uncertainties. Even in the simple case H···H···H the calculated values differ considerably from the observed one, and in other cases the usual simplified treatment predicts the existence of stable molecules H···H···CH_3 and Cl···Cl···Cl, for which there is no experimental evidence (Gorin, *Acta Physicochim. U.R.S.S.*, 1938, **9**, 691; Gorin, Kauzmann, Walter, and Eyring, *J. Chem. Physics*, 1939, **87**, 633; Rollefson and Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 2661). We are therefore unable to attach much weight to the calculations given by Syrkin

and Diatkina (*loc. cit.*) for the resonance link in the boron hydrides, since they depend on similar simplifying assumptions and do not take into account the repulsion between electrons attached to different atoms. In particular, we do not believe that there is yet sufficient evidence to prefer either the covalent structures (IV*a*) or the ionic structures (IV*b*) as representing the state of the resonance link. Either set represents an equivalent pair of bond assignments and will lead to a resonance stabilisation: on the other hand, appreciable resonance between the two sets will only occur if their energies happen to be close enough together. The ionic structures do not conflict with the high volatility of the boron hydrides, since the resonance hybrid will have no dipole moment.

An apparent difficulty connected with the bridge configuration is the close approach of the two boron atoms. If the B···H links are not to be much longer than the normal B–H distance, the distance between the two borons cannot exceed about 2 A., and electron-diffraction measurements do in fact give a value of 1·8 A. for this distance in diborane (see below). The closest distance of approach of two unlinked atoms is usually taken as 3·0—3·5 A., and the energy expended against repulsive forces in reducing this distance to 1·8 A. would be so great as to out-weigh the resonance stabilisation. We believe, however, that this difficulty is only an apparent one. The experimental evidence on the repulsion of unlinked atoms relates mainly to atoms having unshared electrons in their outer shells (*e.g.*, –Cl, >O, ⩾N) and to directions of approach far removed from the bonds attached to these atoms. Under these conditions the repulsion is chiefly due to the unshared electrons. On the other hand, in every resonating structure proposed for the boron hydrides the boron atoms have no unshared electrons in their outer shells, and the electron density in the line joining the two borons will be low: hence the repulsion between them will be much lower than in the general case of unlinked atoms. There will, of course, be repulsion between the nuclei and between the *K*-shells of electrons, but the radius of the latter in boron is only about 0·12 A. (cf. Bartlett and Dunn, *Physical Rev.*, **1933**, **44**, 296). It is therefore quite reasonable to suppose that the two unlinked boron atoms in the bridge can approach to a distance of 1·8 A. without any great expenditure of energy.

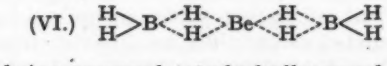
The same kind of consideration explains why the resonance bridge link is not formed by other hydrides, notably ammonia, water, and hydrogen fluoride. If a hypothetical dimeric bridge structure is written for any of these compounds, *e.g.*, (V), it will be found that every resonance form contains one or more pairs of unshared electrons on the central atoms. The resulting repulsion renders the bridge structure impossible, and the polymerisation of these hydrides therefore takes place only by the familiar "hydrogen bond," giving chain polymers of indefinite length. In other cases, *e.g.*, methane and hydrogen sulphide and chloride, there is no appreciable polymerisation by either mechanism.

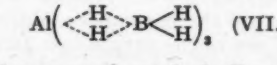


(V.)

In general, we should expect to find polymerisation by the resonance bridge mechanism in any covalent hydrides XH, XH_2, or XH_3 having no unshared electrons in the outer shell. These hydrides would occur in the first three groups of the periodic table, or among the transition and rare-earth elements. Until recently, boron was the only element known to form covalent hydrides fulfilling the necessary conditions, but a volatile gallium hydride, Ga_2H_6, has now been reported having properties very similar to those of diborane (Wiberg and Johansen, *Angew. Chem.*, **1942**, **55**, 38). The only other well-defined hydrides formed in the appropriate part of the periodic table are salt-like in character (*e.g.*, Li^+H^-), so the resonance bridge hypothesis thus accounts satisfactorily for the unique position occupied by the boron and gallium hydrides. Some indications of hydride formation have been observed in the action of atomic hydrogen on the elements silver, copper, gold, beryllium, indium, and thallium (Pietsch, *Z. Elektrochem.*, **1933**, **39**, 577), the products being non-volatile (except in the last two cases) and stable at fairly high temperatures. They are decomposed by water with the evolution of hydrogen and were regarded by Pietsch as salts containing the anion H^-. However, it seems unlikely that these relatively noble metals should form stable hydrides of a type so far known only for the strongly electropositive alkali and alkaline-earth metals, and it is possible that the products obtained are covalent hydrides polymerised through a bridge linkage. It may be noted that a hydride XH_2 containing no unshared outer electrons can polymerise by resonance bridges to form long-chains polymers of indefinite length, while XH and XH_3 are limited to dimerisation.

Aluminium hydride has not been prepared in a pure state, although according to Wiberg and Stecher (*Angew. Chem.*, **1939**, **52**, 372) there is little doubt that it is dimeric. Moreover, both beryllium and aluminium form well-defined volatile mixed hydrides with boron, BeB_2H_8 and AlB_3H_{12} (Schlesinger *et al.*, *J. Amer. Chem. Soc.*, **1940**, **62**, 3421, 3425, 3429). Hitherto, two types of structure have been proposed for these compounds, first, the ionic structures $Be^{++}(BH_4^-)_2$ and $Al^{+++}(BH_4^-)_3$, and secondly, resonance covalent structures involving single-electron links in which boron has a covalency of five. Although the salt-like compound $LiBH_4$ undoubtedly has an ionic structure, such a structure seems inappropriate for the most volatile beryllium and aluminium compounds known, and a covalency of five is not met with in other boron compounds, or elsewhere in the first short period. In terms of the bridge linkage these compounds appear naturally as (VI) and (VII),

(VI.) 



(VII.)

the valencies being arranged tetrahedrally round beryllium and boron, and octahedrally round aluminium. This disposition of valencies predicts that the three boron atoms in AlB_3H_{12} will be at the vertices of an equilateral triangle with the aluminium at the centre, as is found by electron diffraction (Beach and Bauer, *J. Amer. Chem. Soc.*, 1940, **62**, 3440). The bridges in these compounds can be interpreted in terms of resonance

structures analogous to those for diborane : for example, in BeB_2H_8 we have the possibilities (VIII, *a*, *b*, and *c*). [The four covalent bond assignments in (VIII*a*) are actually all equivalent, and the apparent difference between

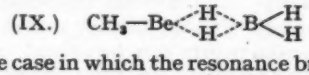
(VIII*a*.)

(VIII*b*.)

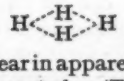
(VIII*c*.)

the first and second pairs is due to the planar representation employed.] The unstable compound $CH_3{\cdot}BeBH_4$ can be similarly formulated as (IX).

(IX.)



(X.)



There is only one case in which the resonance bridge link fails to appear in apparently favourable circumstances, and that is in hydrogen itself, where the structure (X) might be expected. (The formation of H_4 from $2H_2$ must actually be considerably endothermic, since the conversion of para- into ortho-hydrogen does not take place appreciably by direct interchange between two hydrogen molecules.) We have already seen that H···H···H only just fails to be a stable molecule, and the distinction between the existence of B_2H_6 and the non-existence of H_4 may depend only on the relative magnitude of exchange and repulsion energies. On the other hand, H_4 can only be formulated in terms of covalent bond assignments, since the analogous resonance structure to $BH_2^+BH_4^-$ would be $H^+H_3^-$, which cannot exist. This suggests that a resonance link may only be stable when it is formed partly or entirely from ionic structures, which can be achieved by the simple and mixed boron hydrides, but not by hydrogen itself.

Physical Evidence for the Structure of Diborane.—The evidence discussed in this section relates chiefly to the disposition of the boron and hydrogen atoms in space, and is largely independent of particular assumptions about the nature of the links involved. We consider that, as a whole, it favours the bridge configuration rather than one resembling ethane.

Electron diffraction. Electron diffraction by gaseous diborane has been studied by Bauer (*J. Amer. Chem. Soc.*, 1937, **59**, 1096), who originally interpreted his observations on the basis of the ethane model and obtained 1·86 A. and 1·27 A. for the B–B and the B–H distance respectively. These distances are larger than the expected single-bond values, which lent support to the idea of one-electron or " no electron " bonds. More recently, Bauer has compared his results with the bridge structure (*Chem. Reviews*, 1942, **31**, 43, and private communication from the author; cf. also Diatkina and Syrkin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **35**, 180). The qualitative features of the observed curve are predicted equally well by the ethane structure and by the bridge structure, except that the latter fails to predict the faint inner peak observed at small scattering angles. When the calculated positions of maxima and minima are compared with the observed ones, agreement is good for both models, except that the unresolved maximum observed at $s = 11{\cdot}9$ is predicted more correctly by the bridge model ($s = 12{\cdot}1$) than by the ethane model ($s = 13{\cdot}2$). For the remaining maxima and minima the mean deviations are 1·7% and 1·9% for the bridge and for the ethane structure, respectively. The results of electron diffraction thus do not lead to any clear-cut decision between the two structures. Bauer considers that the bridge structure can be eliminated on account of its failure to predict the faint inner peak, but in view of the other arguments advanced in this paper we shall not regard this objection as final.

The dimensions derived by Bauer for the bridge structure accord well with its formulation as a resonance linkage. He finds 1·79 A. for the distance between the two boron atoms, terminal B–H = 1·18 A., ring B···H = 1·39 A., terminal angle H–B–H = 120°, ring angle H···B···H = 100°. The terminal B–H distance agrees within the experimental error with the value 1·21 A. given by Bauer and Beach (*J. Amer. Chem. Soc.*, 1941, **63**, 1394) and with 1·20 A. found experimentally in the compound $H_3\overset{-}{B}{\cdot}\overset{+}{C}O$ (Bauer, *ibid.*, 1937, **59**, 1804). On the other hand, the B···H distance in the ring is greater than this, as would be expected for a resonance link having only one-half single-bond character. The repulsion between the boron atoms has lowered the ring angle to somewhat less than the normal tetrahedral angle, and there is a corresponding increase in the terminal angle. Bauer (*Chem. Reviews*, 1942, **31**, 46) has used these dimensions as an argument against the bridge structure, but he assumes that the boron atoms are connected directly by a link as well as indirectly through the hydrogens, which leads to an unacceptable orientation of five valencies round each boron.

Electron bombardment. Hipple (*Physical Rev.*, 1940, **57**, 350) has found that when diborane is bombarded with electrons, the ions formed include B_2^+ and B_2H^+, and the formation of these two species has been quoted

as strong evidence against the bridge structure (Bauer, *loc. cit.*, p. 72). However, it should be noted that each of the ions $B_2H_3^+$, $B_2H_2^+$, B_2H^+ and B_2^+ contains enough electrons to form normal electron-pair links throughout. Either type of resonance link (one-electron or bridge) would be replaced by normal links as soon as enough hydrogen atoms had been removed from the diborane molecule, and the formation of the observed ions thus gives no information about the structure of diborane itself.

Vibrational spectrum. Both the Raman and the infra-red spectrum of diborane have been observed (Anderson and Burg, *J. Chem. Physics*, 1938, **6**, 586; Stitt, *ibid.*, 1941, **9**, 780) and their interpretation in terms of the ethane model has been attempted, though with little success. The infra-red spectrum is far more complicated than that of ethane, and in particular, there are too many strong lines of low frequency which cannot be regarded as overtones or combination tones and will not fit into any theoretical scheme. In order to meet this difficulty, Stitt (*loc. cit.*) has postulated the existence of one or more low-lying electronic levels, and gives two tentative assignments of frequencies on this basis. However, there is no independent evidence for the existence of these levels in diborane or in any similar molecules, so the explanation is hardly convincing. The same difficulty appears in a simple form in the Raman spectrum, where the two most intense lines are at 2102 and 2523 cm.$^{-1}$. From their intensity they must be fundamental vibrations of a completely symmetrical type, and their frequencies both lie in the range expected for stretching vibrations of the B–H link. However, the ethane-like structure predicts only *one* symmetrical type of B–H stretching vibration, and Anderson and Burg (*loc. cit.*) could only suggest that this pair of lines might be due to a resonance splitting, although the difference of 421 cm.$^{-1}$ is about 10 times as great as the normal separation of a resonance pair.

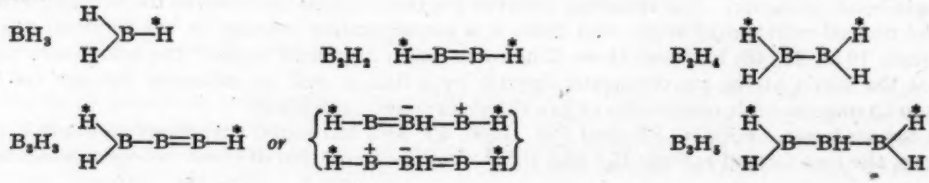
The vibrational spectrum can be explained without difficulty on the basis of the bridge structure for diborane. (This fact is mentioned by Stitt, *loc. cit.*, but dismissed without further consideration.) We shall publish elsewhere a complete vibrational analysis, but the main points can be stated briefly. The bridge molecule has the same symmetry characteristics as ethylene (three perpendicular planes of symmetry), and none of its vibrational modes is degenerate. There are hence 18 distinct vibrational frequencies (compared with 12 for ethane), of which 9 can appear in the Raman spectrum, 8 in the infra-red, and one is inactive. Moreover, since there are two different kinds of B–H binding, the number of frequencies in the range corresponding to bond-stretching is twice as great as for ethane. This increase in the number of fundamental frequencies clears away the difficulties encountered with the ethane model, and in particular, the two intense Raman lines 2523 and 2102 cm.$^{-1}$ can be pictured (somewhat crudely) as due to symmetrical stretching vibrations of the terminal B–H groups and the ring respectively. The observed vibrational spectrum thus lends strong support to the bridge configuration, and constitutes probably the strongest single piece of evidence in its favour.

Specific heat. The specific heat of diborane has been measured between 95° and 324° K., and gives evidence of hindered rotation about the B–B axis (Stitt, *J. Chem. Physics*, 1930, **8**, 981). Assuming an ethane-like structure and a sinusoidal potential barrier, Stitt calculated the height of this barrier to be 4000—6000 cals./mole, compared with 3000 cals. for ethane itself. Later calculations taking into account the supposed low electronic levels gave still higher values for the height of the barrier (*idem, loc. cit.*, 1941). Hindered rotation in ethane and similar molecules has been attributed either to interaction between the hydrogen atoms or to partial double-bond character in the central link. If ethane and diborane are similar molecules, it is remarkable on either hypothesis that there should be greater hindrance to rotation in diborane, since the hydrogens are further apart than in ethane, and double-bond formation between the borons is much less probable. On the other hand, the bridge structure automatically explains the resistance to rotation, and although the torsional oscillation cannot appear directly in the infra-red or Raman spectra, it should be possible to calculate its frequency from those of the other bending vibrations.

Crystal structure. The work of Mark and Pohland (*Z. Kryst.*, 1925, **62**, 103) on the structure of solid diborane is sometimes quoted as demonstrating its similarity to ethane. Actually, the *X*-ray observations give information only about the positions of the boron atoms in the lattice, and the further data given are deduced by assuming that the hydrogen atoms have the same arrangement as in ethane. Hence, although the crystal evidence is consistent with the ethane model, it provides no criterion for deciding between this and the bridge structure.

The Higher Hydrides of Boron.—There is little detailed physical information about these compounds, and we shall only show how far the bridge structure is able to predict or account for the formulæ of the hydrides so far known. There are many possibilities, and the structures given are intended only as suggestions. All the hydrides can be built up from " borines," which have normal electronic structures with tervalent boron but contain >B–H groups which can unite two borines by means of a bridge. The first few borines can be formulated as follows, an asterisk indicating a free >B–H. It should be noted that a given BH_2 or $-BH_2$ group can only take part in one resonance bridge, and we have also supposed that the group >B–BH–B< in B_3H_5 shows no tendency to polymerise.

Borines.



This leads to the following formulæ for possible boranes containing six or fewer boron atoms, a semicolon being used to indicate a bridge linkage between two borines. The structures proposed contain no groups capable of further polymerisation, and are the only ones which can be constructed from borines containing up to three boron atoms.

Boranes.

B_2H_6	$BH_3;BH_3$	(B_4H_8)	$BH_3;B_2H_2;BH_3$	B_4H_{10}	$BH_3;B_2H_4;BH_3$
B_3H_9	$BH_3;B_2H_3;BH_3$	B_5H_{11}	$BH_3;B_2H_5;BH_3$		
B_4H_{10}	$BH_3;B_2H_2;B_2H_2;BH_3$	B_6H_{12}	$BH_3;B_2H_2;B_2H_4;BH_3$		
(B_6H_{14})	$BH_3;B_2H_4;B_2H_4;BH_3$				

This list includes all the known hydrides of boron except $B_{10}H_{14}$, and only two (B_4H_8 and B_6H_{14}) which do not correspond to known compounds. The bridge structure is thus reasonably successful in predicting the formulæ of the simpler boranes, and it may be particularly noted that no hydrides containing three boron atoms can exist on this hypothesis. If the list of borines is extended it is possible to write alternative structures for the last three hydrides, but not to formulate any new ones containing 6 or fewer boron atoms. Many higher boranes can be formulated, including $B_{10}H_{14}$, the only hydride with more than 6 boron atoms yet isolated.

Electron-diffraction studies have been carried out with B_4H_{10}, B_5H_9 and B_5H_{11} (Bauer and Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 2403; Bauer, *ibid.*, 1938, **60**, 805), and the results interpreted in terms of the one-electron resonance hypothesis. However, other possibilities are not excluded, and it would be of interest to compare the experimental curves with those derived from the bridge formulæ given above.

Our thanks are due to Professor S. H. Bauer for sending us details of his electron-diffraction calculations for diborane, and to Dr. L. E. Sutton for helpful discussion.

BALLIOL COLLEGE, OXFORD. [*Received, February 4th*, 1943.]

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65. *A Criterion for the Mechanism of the Reaction between Alkyl Halides and Hydroxylic Solvents. Part III.* Reactions of* n*-Butyl Bromide.*

By MARJORIE L. BIRD, EDWARD D. HUGHES, and CHRISTOPHER K. INGOLD.

A means of distinction between the two homogeneous mechanisms of nucleophilic substitution, suitable for application to those first-order reactions in which the reagent is in large excess, has been based on the circumstance that in bimolecular substitution the product is determined in a single reaction stage, of which the rate can be measured, whilst in unimolecular substitution it is formed, not in the rate-measured stage, but in a subsequent fast stage :

$$Y + R|{-}X \longrightarrow Y{-}R + X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_N2)$$

$$\left.\begin{array}{l} R|{-}X \longrightarrow R^+ + X \text{ (slow)} \\ Y + R^+ \longrightarrow Y{-}R \text{ (fast)} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_N1)$$

Olson and Halford having advanced a successful two-constant expression for the calculation of reaction rates in binary solvent mixtures, Bateman, Hughes, and Ingold pointed out that the principle stated could be applied as follows. Consider the simultaneous hydrolysis and alcoholysis of an alkyl halide in aqueous alcohol. Independently of mechanism, the two constants that can be derived by means of Olson and Halford's equation from rate measurement in two solvent mixtures of different composition will permit calculation of the rate in a mixture of some other composition. If the mechanism is bimolecular, the same two rate-derived constants will also allow calculation of the composition of the substitution product (alcohol plus ether), because this is formed in the reaction whose rate is measured, whereas if the mechanism is unimolecular, the measured rates will have no connexion with the composition of the product, which is formed in a separate reaction-stage. It had previously been shown by Bateman, Hughes, and Ingold that the same pair of constants could not be used to calculate both rates and product compositions for the solvolysis of *tert.*-butyl chloride in aqueous alcohol, consistently with earlier conclusions that these reactions are unimolecular. It is now shown that a single pair of constants permits a successful calculation of both rates and product compositions for the corresponding solvolysis of *n*-butyl bromide, consistently with previous conclusions that these reactions are bimolecular. The calculated data agree with the experimental determinations to within the limits of accuracy of the latter. The method has thus been demonstrated with respect to both the types of result to which it can lead.

THIS paper contributes to the third of the six methods (listed by Hughes, *Trans. Faraday Soc.*, 1941, **37**, 611) which have been developed, especially in relation to solvolytic substitutions, for distinguishing between the bimolecular and the unimolecular mechanism of nucleophilic substitution. The method utilises effects produced by changes of solvent, and in the particular form with which we are here concerned, it depends on effects arising in mixtures of reactive solvents. The substitution to be used in illustration is the solvolysis, including the hydrolysis and alcoholysis, of alkyl halides in hydroxylic solvents. In the example of hydrolysis the mechanisms are as follows :

$$RX + H_2O \longrightarrow R{\cdot}OH + H^+ + X^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_N2)$$

$$\left.\begin{array}{l} RX \longrightarrow R^+ + X^- \text{ (slow)} \\ R^+ + H_2O \longrightarrow R{\cdot}OH + H^+ \text{ (fast)} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_N1)$$

* Part I, J., 1938, 881; Part II, *J. Amer. Chem. Soc.*, 1938, **60**, 3080.

The method here developed was first suggested by an investigation by Olson and Halford (*J. Amer. Chem. Soc.*, 1937, **59**, 2644), who, believing all solvolysis to be bimolecular, sought to establish their view in the example of the solvolysis of *tert.*-butyl chloride, by applying an activity rate equation to the solvent, as well as to the solute, in a kinetic test for bimolecularity. For solvolysis by mixtures of alcohol and water, their equation for the rate was

$$\text{Rate} = (k_a p_a + k_w p_w) p_{RX} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the subscripts *a*, *w*, and RX denote respectively alcohol, water, and the alkyl halide, and the *p*'s represent partial vapour pressures. The symbols k_a and k_w denote kinetic constants, and Olson and Halford showed that, if these are determined by measurement of the rate of solvolysis at two extremes of solvent composition, then the equation satisfactorily expresses the rate of solvolysis at any intermediate solvent composition. On this evidence they concluded that the solvolytic reactions were indeed bimolecular. Then Bateman, Hughes, and Ingold pointed out (J., 1938, 881) that the success of equation (1) as an interpolation formula for rates is not dependent on the assumed bimolecular mechanism, and that it could constitute an equally useful instrument for application to the rates of unimolecular reactions; but that an effective procedure for deriving conclusions relative to mechanism consisted in determining whether or not the same pair of constants, k_a and k_w, which are required to express rates of solvolysis by means of equation (1), would also correctly reproduce the proportions of the products when inserted in equation (2), namely,

$$\text{ROAlk}/(\text{ROAlk} + \text{ROH}) = k_a p_a/(k_a p_a + k_w p_w) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

ROAlk and ROH are here the quantities of the ethereal and the alcoholic products, formed respectively from the solvent constituents Alk·OH and H_2O by interaction with the alkyl halide RX. According to Olson and Halford's assumptions, the rate-derived constants should be applicable in equation (2), rates and products being determined in a single bimolecular reaction stage. The same pair of constants should, however, be in principle incapable of use for the calculation of both rates and product compositions if the mechanism is unimolecular, rates and products being in this case determined in different reaction stages. In the example of *tert.*-butyl chloride large discrepancies resulted when this test for bimolecularity was applied, consistently with the conclusion, previously reached on other grounds, that the solvolysis of this substance in aqueous media was unimolecular.

The mechanism of the aqueous solvolysis of *tert.*-butyl chloride has since then passed out of the stage of controversy, and we return to the subject only in order more completely to establish the general method of determining reaction mechanism; for Bateman, Hughes, and Ingold's work was incomplete in one respect: they certainly noted that, if the solvolytic reaction had been bimolecular, then, according to Olson and Halford's theory, equations (1) and (2) should have been consistently applicable, but they did not show that these equations are in fact consistently applicable in the case of a solvolysis which is admittedly bimolecular. A complementary experimental demonstration of this nature is evidently necessary for the establishment of the method.

It is already clear from earlier criteria that all the simpler primary alkyl halides undergo solvolysis in aqueous alcohol by the bimolecular mechanism (Hughes and Ingold, J., 1935, 244; cf. Bateman, Cooper, Hughes, and Ingold, J., 1940, 925). *n*-Butyl bromide was chosen for the present investigation, because it belongs to this class of halide, and because methyl *n*-butyl and ethyl *n*-butyl ethers could be estimated by the technique which Bateman, Hughes, and Ingold had developed for the corresponding *tert.*-butyl alkyl ethers.

The solvolysis of *n*-butyl bromide has been studied at 59·4° in methyl alcohol and in five mixtures of methyl alcohol and water; and also at 75·1° in ethyl alcohol and three mixtures of ethyl alcohol and water. In each case the first-order rate constant for solvolysis was determined, together with the "Henry's law constant" connecting the partial vapour pressure of *n*-butyl bromide with its concentration; the partial vapour pressures of the solvent constituents were already known from the work of Wrewsky (*Z. physikal. Chem.*, 1913, **81**, 17). In each case also the proportion was determined in which methyl *n*-butyl or ethyl *n*-butyl ether was formed. A very few units % of the *n*-butyl bromide became converted into Δ^1-butene, and this proportion was estimated in a distributed selection of cases. The proportion of *n*-butyl alcohol being thence obtained by difference, all the data were available which were needed for the determination of mechanism.

As to the calculations, it is necessary to remark only that, since it is more convenient to deal with first-order rate constants than with instantaneous rates, the rate equation (1) is for practical purposes replaced by an equivalent specific rate equation, obtained by division throughout by the concentration of alkyl halide:

$$\text{Specific rate} = \frac{\text{Rate}}{[\text{RX}]} = k_1 = (k_a p_a + k_w p_w)\frac{p_{RX}}{[\text{RX}]} = (k_a p_a + k_w p_w) H_{RX} \quad . \quad . \quad (1')$$

Here H_{RX} is the "Henry's law constant" of the alkyl halide, defined for convenience as the partial vapour pressure divided by the molar concentration. All partial vapour pressures are expressed in mm. of mercury. The units of the kinetic constants k_a and k_w are (sec.$^{-1}$) (g.-mol./l.) (mm. Hg.)$^{-2}$. Specific rates are in sec.$^{-1}$. For each series of solvents, the constants k_a and k_w were obtained from the measured specific rates of solvolysis at the extremes of the investigated range of solvent composition. The following values were found:

Methyl-alcoholic solvents at 59·4° . . . $k_a = 1{\cdot}32 \times 10^{-11}$; $k_w = 3{\cdot}79 \times 10^{-11}$.
Ethyl-alcoholic solvents at 75·1° . . . $k_a = 2{\cdot}10 \times 10^{-11}$; $k_w = 4{\cdot}41 \times 10^{-11}$.

It is shown in Table I that these constants enable the dependence of solvolysis rate on solvent composition to be calculated from equation (1') to within the accuracy of the observational data. (The main error, a few units

%, is contained in the " Henry's law constants," which were determined by aspiration. The first-order rate constants themselves are probably good to 1%).

TABLE I.

Rates of Solvolysis of n*-Butyl Bromide in Aqueous Methyl-alcoholic Solvents at 59·4° and in Aqueous Ethyl-alcoholic Solvents at 75·1°, and Partial Vapour Pressures of the Reaction Components.*

H_2O in solvent.		Observed.				Calc.	H_2O in solvent.		Observed.				Calc.
Wt. %.	Mols. %.	p_a.	p_w.	H_{RX}.	10^7k_1.	10^7k_1.	Wt. %.	Mols. %.	p_a.	p_w.	H_{RX}.	10^7k_1.	10^7k_1.
Methyl-alcoholic solvents at 59·4°.													
0·0	0·0	609	0	47·2	3·8	*	20·0	30·8	439	58	155	13·9	12·5
8·5	14·1	527	30	88·2	7·3	7·2	34·5	48·3	356	80	311	24·2	24·0
16·7	26·3	461	52	147	11·6	11·9	45·8	60·1	302	92	486	36·4	*
Ethyl-alcoholic solvents at 75·1°.													
0·0	0·0	665	0	55·3	7·8	*	33·3	56·2	393	227	323	56·7	58·6
12·0	25·8	513	144	142	24·8	24·3	52·3	73·7	330	243	628	110·8	*

* The corresponding experimental values were used in order to calculate the constants k_a and k_w.

The kinetic constants, thus determined and tested, were next used in order to calculate product compositions for comparison with the compositions found analytically. The quantity calculated was the percentage extent to which the substitution reactions of *n*-butyl bromide proceed in the direction leading to methyl *n*-butyl or ethyl *n*-butyl ether : 100 ROAlk/(ROAlk + ROH). Any butylene formed merely represents so much *n*-butyl bromide diverted from the competing substitution processes. Reference to the experimental section, in which full analytical data are presented, will show that the actual amount of butylene produced is so small that it might have been neglected. However, for the sake of formal consistency we express the analytical results also in terms of the ratio 100ROAlk/(ROAlk + ROH). The comparison between the calculated and observed percentages of ether formed at the temperatures, and in the solvent mixtures, used for the kinetic investigation is shown in the left-hand section of Table II. In conformity with the presumption of a bimolecular mechanism, these values agree to within the error of the analytical determinations (a few units %).

In striking contrast stand the corresponding data obtained by Bateman, Hughes, and Ingold (*loc. cit.*) for *tert.*-butyl chloride, for which the formed proportion of ether was always 2—3 times larger than the proportion calculated. These figures are reproduced in the right-hand part of Table II. It would appear from the comparison that in the relation between solvent composition and product composition we have a very sharp criterion for mechanism.

TABLE II.

Illustrating determination of solvolytic mechanism by solvent variation.

	(S_N2) *n*-Butyl bromide (this paper).			(S_N1) *tert.*-Butyl chloride (B., H., I., 1938).			
		100ROAlk/(ROAlk + ROH).				100ROAlk/(ROAlk + ROH)	
Solvent and temp.	Mols. % of H_2O.	Calc.	Found.	Solvent and temp.	Mols. % of H_2O.	Calc.	Found.
MeOH–H_2O mixtures at 59·4°	14·1	86	88	MeOH–H_2O mixtures at 25·0°	16·4	43	83
	26·3	75	74		28·4	29	68
	30·8	72	72		40·0	17	49
	48·3	61	61				
	60·1	53	51				
EtOH–H_2O mixtures at 75·1°	25·8	63	63	EtOH–H_2O mixtures at 25·0°	26·4	18	53
	56·2	45	50		44·7	11	33
	73·7	39	35		68·3	8	18

However, it must not be forgotten that types of bimolecular reaction may exist for which Olson and Halford's rate equation does not represent so good an approximation as has here been illustrated,* and also that it would

* It has been noted before that equations (1) and (2) can only be approximate. According to the transition state theory, each of the terms $k_a p_a p_{RX}$ and $k_w p_w p_{RX}$ should be divided by the activity coefficient of the appropriate transition state. Bartlett has proposed an approximation in which these activity coefficients are taken as proportional to those of the corresponding solvent constituents, alcohol and water (*J. Amer. Chem. Soc.*, 1939, **61**, 1630). We have applied Bartlett's equations to our data and have obtained a similar general result, in particular, the same type of marked contrast between *n*-butyl bromide and *tert.*-butyl chloride. However, the agreement of Bartlett's formulæ with the experimental data for *n*-butyl bromide is definitely less exact than is that of Olson and Halford's formulæ, with respect both to the rates and to the product compositions. This led us to consider theoretically whether Bartlett's or Olson and Halford's approximation should be regarded as preferable. It is a difficult point on which to reach a definite conclusion, but we may note that both transition states contain hydrophilic quasi-ionic charges (due to the electron transfers), and both contain hydrophobic hydrocarbon radicals; also both contain a hydroxyl group associated with carbon and an extra proton. The combined effect of these features might be to render the activity coefficients somewhat insensitive to solvent composition, a circumstance which would favour Olson and Halford's approximation. In any case, since the common constitutional features mentioned are likely to be the most important determinants of the two activity coefficients, we might expect the latter to behave somewhat similarly, rather than the one behaving like the activity coefficient of water and the other like that of alcohol, as is assumed in Bartlett's approximation.

be possible for some particular unimolecular reaction to simulate accidentally the behaviour to be expected for a bimolecular process. For the one other unimolecular solvolysis for which the relevant investigation has been carried out, albeit incompletely, namely, the solvolysis of benzhydryl chloride, a very clear indication was obtained that a more complete study would have yielded results quite similar to those obtained by Bateman, Hughes, and Ingold for *tert.*-butyl chloride (Farinacci and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2544; Bateman, Hughes, and Ingold, *ibid.*, 1938, **60**, 3080).

Experimental.

Materials.—*n*-Butyl bromide, dried and redistilled, had b. p. 100·5°/765 mm. Absolute methyl and ethyl alcohols were purified and fully dried by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210). Methyl *n*-butyl ether, prepared from *n*-butyl bromide and methyl-alcoholic sodium methoxide, had b. p. 71°/760 mm.; ethyl *n*-butyl ether, similarly obtained, had b. p. 92°/764 mm.

Kinetic Measurements.—Portions of 5 c.c. or 10 c.c. of the original solution of *n*-butyl bromide in the alcoholic or aqueous-alcoholic solvent were enclosed in sealed bulbs, which were immersed in the thermostat for the requisite times, and then cooled, cleaned, and broken under acetone, the liberated hydrobromic acid being finally titrated with sodium hydroxide. In the anhydrous and less aqueous solvents the first-order rate constants began to drift downward some time after the commencement of reaction, due to interaction of the liberated hydrogen bromide with the alcohol of the solvent. However, this disturbance did not enter early enough to interfere with the observation of satisfactory solvolytic rate constants. Table III shows the results of a typical run, and Table IV the summarised results of all the runs.

Table III.

Solvolysis of n-*butyl bromide: Kinetic run No.* 16.

[Solvent: Aqueous ethyl alcohol containing 88·0% by weight = 74·2 mols. % of ethyl alcohol. Temp. = 75·1°. *n*-Butyl bromide initially 0·0925M. Samples of 5·00 c.c. titrated with 0·0428N-sodium hydroxide. $k_1 = (1/t)\ln a/(a-x)$ expressed in hr.$^{-1}$.]

t (hrs.).	Titre (c.c.).	10^3k_1.	t (hrs.).	Titre (c.c.).	10^3k_1.	t (hrs.).	Titre (c.c.).	10^3k_1.	t (hrs.).	Titre (c.c.).	10^3k_1.
0·00	0·00	—	24·6	2·10	8·83	95·7	5·93	8·33	216·0	8·22	6·62
5·45	0·51	8·90	42·9	3·45	8·96	121·1	6·62	7·83	480·0	9·31	4·12
13·50	1·23	8·90	48·2	3·80	9·00	163·6	7·70	7·63	∞	10·80	—
19·10	1·70	8·97	64·7	4·75	8·95						

(The first seven values of k_1 lead to the mean 0·00893 hr.$^{-1}$; the last five values show the incursion of the solvent reaction mentioned in the text.)

Table IV.

Solvolysis of n-*butyl bromide: Summarised results of kinetic experiments.*

[In all runs the *n*-butyl bromide was initially about 0·09M.]

Run No.	H_2O in solvent. Wt. %	H_2O in solvent. Mols. %	No. of 10^3k_1 values averaged.	Range of 10^3k_1 values averaged.	10^3k_1 (k_1 in hr.$^{-1}$). Mean.	Mean.
			Methyl-alcoholic solvents at 59·4°.			
1	0·0	0·0	10	1·34— 1·39	1·37	1·37
2	,,	,,	4	1·35— 1·39	1·37	
3	8·5	14·1	7	2·61— 2·67	2·64	2·64
4	,,	,,	7	2·57— 2·69	2·64	
5	16·7	26·3	7	4·10— 4·27	4·16	4·16
6	,,	,,	5	4·11— 4·19	4·15	
7	20·0	30·8	6	4·96— 5·06	5·00	5·01
8	,,	,,	7	4·94— 5·09	5·02	
9	34·5	48·3	10	8·74— 8·95	8·82	8·83
10	,,	,,	6	8·79— 8·92	8·84	
11	45·8	60·1	3	13·00—13·24	13·10	13·11
12	,,	,,	5	13·00—13·16	13·09	
13	,,	,,	10	13·00—13·20	13·13	
			Ethyl-alcoholic solvents at 75·1°.			
14	0·0	0·0	6	2·78— 2·84	2·80	2·80
15	,,	,,	4	2·80— 2·82	2·81	
16	12·0	25·8	7	8·83— 9·00	8·93	8·91
17	,,	,,	7	8·80— 9·00	8·89	
18	33·3	56·2	11	19·5 —21·3	20·5	20·4
19	,,	,,	5	19·8 —20·6	20·3	
20	52·3	73·7	7	38·8 —40·9	40·2	39·9
21	,,	,,	5	38·9 —40·5	39·7	
22	,,	,,	7	39·0 —40·4	39·9	

Estimations of Methyl n-*Butyl Ether and Ethyl* n-*Butyl Ether.*—The method was essentially the same as that employed by Bateman, Hughes, and Ingold (*loc. cit.*) in the case of the corresponding *tert.*-butyl ethers. The first step is to carry out an "isolation experiment," in which the reaction mixture is fractionated after dilution with water, and the ether isolated as described below; and the next is to proceed with a parallel "recovery experiment" on a synthetic solution corresponding in all respects to the completed reaction mixture, except for the omission of the trace of olefin. Isolation and recovery experiments were carried out for each of the eight aqueous-alcoholic media used in the kinetic runs. For all the aqueous methyl-alcoholic media the recovery of methyl *n*-butyl ether from synthetic solutions was 49 ± 1%;

and from all the aqueous ethyl-alcoholic media the recovery of ethyl *n*-butyl ether was 64—65%. Attempts to increase these figures failed, but repetitions showed that the figures themselves were reliably reproducible.

Original solutions for isolation experiments were each prepared from 1000 c.c. of the aqueous-alcoholic medium and 30·0 c.c. of *n*-butyl bromide. Each solvolysis was allowed to proceed until complete in a flask, immersed to the neck in the thermostat at the temperature of the corresponding kinetic run, and fitted with a reflux condenser stoppered at the top. A few drops of phenolphthalein were added, and the solution was kept only just on the acid side of the neutral point by periodic additions of a solution of sodium hydroxide in the particular aqueous-alcoholic medium employed in the experiment. This was to guard against further reaction by the initially formed solvolysis products. At the end of the period of heating, the solution was diluted with water to 1600 c.c., and fractionated with additions of water, and, in the later stages, of calcium chloride, just as in the former research, the precipitated ether being distilled from fused barium oxide and from potassium, and finally weighed and checked for purity by analysis. B. p.'s were correct and constant to ±0·4° and analyses to ±0·3%; *e.g.*, a weighed sample of methyl *n*-butyl ether had b. p. 70·6—71·4°/760 mm., and on analysis gave C, 68·12, 68·23; H, 13·57, 13·97 (Calc.: C, 68·18; H, 13·72%). Original solutions for the recovery experiments were made from 1100 c.c. of the aqueous-alcoholic medium (the excess of this over the amount used for the isolation experiment representing the volume of sodium hydroxide solution added during the course of the latter), 28 g. of sodium bromide, known weights, determined by the requirements of the corresponding isolation experiment, of *n*-butyl alcohol and of either methyl or ethyl *n*-butyl ether, and a few drops of phenolphthalein. The results are in Table V.

TABLE V.

Estimations of the methyl n-*butyl ether and ethyl* n-*butyl ether formed by solvolysis of* n-*butyl bromide in aqueous methyl alcohol at 59·4° or aqueous ethyl alcohol at 75·1°.*

(In all experiments the initial quantity of *n*-butyl bromide was 0·277 g.-mol.)

Solvent and temp.	H_2O in solvent. Wt. %.	H_2O in solvent. Mols. %.	Isolated ether (g).	Mean recovery % (by expt.).	Ether formed. Mols. %.	Ether formed. Mean.
MeOH + H_2O at 59·4°	8·5	14·1	10·2	48	87	87
	16·7	26·3	9·0	50	74	73
			8·7		71	
	20·0	30·8	8·4	48	72	71
			8·3		71	
	34·5	48·3	6·8	48	58	60
			7·2		62	
	45·8	60·1	6·0	49	50	51
			6·1		51	
EtOH + H_2O at 75·1°	12·0	25·8	11·0	65	60	61
			11·4		62	
	33·3	56·2	8·9	64	49	49
			9·0		50	
	52·3	73·7	6·4	64	35	35

Estimations of Olefin.—It has been recognised in the course of previous work that, in solvolytic reactions which become acidic, any olefin formed may partly or wholly disappear again on account of an acid-catalysed addition to it of solvent molecules (Cooper, Hughes, and Ingold, J., 1937, 1280; Hughes and MacNulty, *ibid.*, p. 1283). Therefore, in order to determine the proportion in which an olefin is formed, it is in general necessary to follow the variations in its concentration from the commencement of reaction. For a certain time the amount of olefin present will bear a constant ratio to the amount of the original material destroyed: this constant value must represent the proportion in which the olefin is formed. At some stage, however, the ratio will begin to fall, even though the absolute amount of olefin present may for a time continue to rise; still later, the absolute amount will fall: the effects are successive consequences of the attack of solvent molecules on the first-formed olefin. If we are interested only in the formation of olefin, and not in its reactions, measurements may be stopped as soon as the above-mentioned ratio begins to depart from constancy.

These principles being employed, olefin production in the solvolysis of *n*-butyl bromide, in the solvents and at the temperatures employed for the kinetic runs, was estimated by the sealed-bulb method described in connexion with the kinetic measurements, with the exception that two bulbs were needed for each point on the record of olefin development, one for the alkalimetric estimation of the amount of *n*-butyl bromide destroyed, and the other for the estimation, by bromine addition, of the amount of olefin present. The latter measurement was made by cooling the bulb in a freezing mixture of solid carbon dioxide and alcohol, drying it, and breaking it under a mixture of carbon tetrachloride (60 c.c.) and ice-water. The mixture was shaken, and the carbon tetrachloride layer was first dried for 5 mins. with calcium chloride, and then treated with a solution of bromine in carbon tetrachloride nearly saturated with hydrogen bromide. After 5 mins. had been allowed for the interaction, the residual bromine was estimated by titration with thiosulphate after the addition of potassium iodide and water. The bromine solution was similarly standardised just before and just after the 5-min. interval allowed for the reaction. The results of a typical determination are recorded in Table VI, and a summary of all the values obtained is given in Table VII.

TABLE VI.

Olefin development in solvolysis of n-*butyl bromide: Olefin run No. 5.*

(Solvent: Aqueous ethyl alcohol containing 66·7% by weight = 43·8 mols. % of ethyl alcohol. Temp.: 75·1°. *n*-Butyl bromide initially 0·0927M. Samples of 5·00 c.c. titrated with 0·0428N-sodium hydroxide. Bromine uptake by samples of 5·00 c.c. measured by titration with 0·0455N-thiosulphate.)

Bu^aBr destroyed (equiv. c.c. NaOH)	0·91	1·88	4·60	6·47
,, ,, (% of initial Bu^aBr)	8·4	17·4	42·5	59·9
C_4H_8 present (equiv. c.c. $Na_2S_2O_3$)	0·03	0·06	0·15	0·14
,, ,, (% of initial Bu^aBr)	0·15	0·30	0·75	0·70
,, ,, (% of Bu^aBr destroyed)	1·8	1·7	1·8	1·2
,, formed (% of Bu^aBr destroyed)		1·8		—

TABLE VII.

Olefin formation in solvolysis of n-*butyl bromide : Summarised results.*

(In all runs the *n*-butyl bromide was initially about 0·09M.)

Methyl-alcoholic solvents at 59·4°.				Ethyl-alcoholic solvents at 75·1°.			
Run No.	H_2O in solvent. Wt. %.	H_2O in solvent. Mols. %.	Percentage in which Bu^nBr is converted into C_4H_8.	Run No.	H_2O in solvent. Wt. %.	H_2O in solvent. Mols. %.	Percentage in which Bu^nBr is converted into C_4H_8.
1	8·5	14·1	1·7	4	12·0	25·8	2·7
—	16·7	26·3	(1·5) *				
2	20·0	30·8	1·4	5	33·3	56·2	1·8
—	34·5	48·3	(1·1) *				
3	45·8	60·1	0·8	6	52·3	73·7	1·2

* Interpolated from the other results and used in the calculations in Table II.

It may be pointed out that the reason why we do not care what happens to the olefin, even though its reactions may lead to a *n*-butyl alkyl ether, is because in the estimation of these ethers we took the precaution of maintaining a nearly neutral solution in order (amongst other things) to block any route to the ethers other than that of direct solvolysis of the *n*-butyl bromide. Thus our estimates of ether, like that of olefin, and therefore like that of *n*-butyl alcohol by difference, represent what we require, namely, the quantities of these materials that are directly formed from *n*-butyl bromide, undisturbed by any interconversion of products subsequently to their formation. Since none of the reactions which interconvert the products consumes or produces hydrion, they do not disturb the kinetic measurements.

Partial-pressure Determinations.—The partial pressures of *n*-butyl bromide in the solvents, and at the temperatures, employed for the kinetic measurements were determined by aspiration. The apparatus consisted essentially of a helical spiral, made from glass tubing 20 mm. in diameter, which was held on an upright axis in the thermostat, and was provided with an internally projecting capillary air inlet at the lower extremity, and with delivery arrangements at the upper. The helix was of such a length that when charged with 350 c.c. of the solution to be examined there was adequate free space at the upper end. It was necessary so to adjust the size of the capillary and the pitch of the helix that, on aspiration, a fairly copious procession of small bubbles was produced, which did not overtake one another on their way up the helix. Too high a pitch reduces the time available for the saturation of the bubbles; too low a pitch causes them to coalesce; the latter occurrence also resulted from too high a flow-rate, and too low a flow-rate gave opportunity for the composition of the solution to change by solvolysis during the course of the measurement. The upper end of the helix led successively to a small bulb and a U-tube, intended to catch splashes of liquid, and then to an inverted U-tube, the bend of which, projecting above the bath liquid, carried the delivery tube over the side of the thermostat to the male part of a ground joint. The part of this delivery tube which extended from the thermostat liquid to a point well past the top of the bend was provided with an electrical winding, by means of which it could be heated to about 100° during the course of a determination in order to prevent premature condensation. The only other part of this jointless all-glass unit which projected from the thermostat was the tube leading to the capillary inlet. This tube was connected at its upper end, through a ground joint, to the air-purifying train. By means of the ground joint at the delivery end of the helical unit, connection was made to a trap for the condensation of the aspirated vapour. Thence the gas line led through drying tubes to a calibrated aspirator, a branch being provided to accommodate a manometer.

The solution having attained the temperature of the thermostat, the condensation trap was replaced by a plain piece of tubing, and aspiration was started, in order to sweep out the delivery end of the apparatus and attain steady conditions. Then the trap, cooled in solid carbon dioxide and alcohol, was put into place, and about 50—150 c.c. of air, measured as to pressure and volume, were drawn through the apparatus. The trap was then detached, and fitted with a reflux condenser, and the condensate was boiled with a measured volume of standard alcoholic silver nitrate. The condensed *n*-butyl bromide was thus estimated by the disappearance of silver ion, as subsequently determined by titration with thiocyanate.

TABLE VIII.

Partial vapour pressures of 0·0927M-n-*butyl bromide in aqueous methyl- and ethyl-alcoholic solutions.*

Wt. % H_2O.	Mols. % H_2O.	*v* (c.c.).	*p* (mm.).	v_{RX} (c.c.).	p_{RX} (mm.).	Mean (mm.).	Wt. % H_2O.	Mols. % H_2O.	*v* (c.c.).	*p* (mm.).	v_{RX} (c.c.).	p_{RX} (mm.).	Mean (mm.).
Methyl-alcoholic solvents at 59·4°.													
0·0	0·0	94	727	3·38	4·09	4·37	20·0	30·8	81	730	6·16	16·5	14·4
		93	734	3·42	4·42				101	730	5·62	12·3	
		100	734	3·74	4·50								
8·5	14·1	100	726	5·34	8·57	8·18	34·5	48·3	104	728	11·40	28·9	28·8
		73	726	3·52	7·79				103	728	11·70	29·5	
		73	726	3·52	7·78				80	728	8·51	28·1	
16·7	26·3	102	733	7·10	14·3	13·65	45·8	60·1	102	723	15·90	44·4	45·0
		100	733	7·09	14·6				102	723	16·48	45·8	
		100	738	6·40	13·1				101	730	15·80	45·5	
		98	738	6·02	12·6				102	730	15·55	44·5	
Ethyl-alcoholic solvents at 75·1°.													
0·0	0·0	187	716	21·65	5·08	5·13	33·3	56·2	125	733	43·70	29·2	29·9
		187	716	21·80	5·12				56	733	20·35	30·1	
		140	724	13·82	5·12				55	732	20·40	30·3	
		140	724	14·05	5·20								
12·0	25·8	78	733	16·49	13·10	13·15	52·3	73·7	70	730	41·00	58·2	58·2
		82	733	17·20	13·20				80	730	47·10	58·2	
		100	717	28·10	13·15								

If a volume, *v* c.c., of dry air is saturated at *t*° and *p* mm. pressure, and if the condensate contains w_a, w_w, and w_{RX} g. respectively of (methyl or ethyl) alcohol, water, and *n*-butyl bromide, the molecular weights of these substances being

m_a, m_w, and m_{RX} respectively, then the total volume after saturation will be $(v + v_a + v_w + v_{RX})$ c.c., where $v_a = 22400(t + 273) \times 760w_a/273pm_a$; analogous expressions hold for v_w and v_{RX}. The partial pressures of the constituent vapours will be $p_a = pv_a/(v + v_a + v_w + v_{RX})$ mm., the formulæ for p_w and p_{RX} being similar. Eliminating v_a and v_w among these equations, we find $p_{RX} = v_{RX}(p - p_a - p_w)/(v + v_{RX})$ mm. Here p and v are directly measured, v_{RX} follows from the measured w_{RX}, and p_a and p_w from Wrewsky's results.

In all experiments the initial concentration of *n*-butyl bromide was 0·0927M. Corrections for the diminution of concentration during the course of a measurement, either through solvolysis or through aspiration itself, were too small to be worth applying. The results are in Table VIII.

The corresponding " Henry's law constants " are obtained from the partial pressures by division by 0·0927, the molarity of the *n*-butyl bromide. These values, together with the partial pressures p_a and p_w, are listed in Table I.

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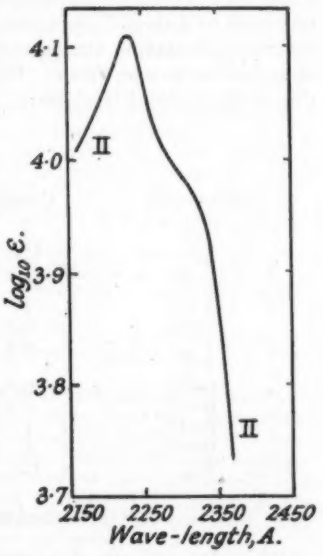
66. *Studies in the Polyene Series. Part VIII. A New Anionotropic Rearrangement. Isomerisation of Ethynylcarbinols from αβ-Unsaturated Aldehydes.**

By E. R. H. JONES and J. T. MCCOMBIE.

A new anionotropic rearrangement, typified by the conversion of propenylethynylcarbinol (I) into *hex*-3-*en*-5-*yn*-2-*ol* (II) in the presence of acid reagents, is reported, and a detailed account given of the isomerisation of (I) under varied experimental conditions. Several other examples are provided, and the constitutions of the rearranged carbinols are rigidly proved. The conjugated vinylacetylene group present in the latter is found to exhibit characteristic light absorption of high intensity in the ultra-violet. The effect of certain substituents on the mobility of the anionotropic system is indicated, but no final conclusions can be drawn from the semi-quantitative data so far available.

IN connection with the programme outlined in Part V (Heilbron, Johnson, Jones, and Spinks, J., 1942, 727) for the synthesis of vitamin A and analogues, a systematic examination of the properties of propenylethynylcarbinol and other ethynylcarbinols from αβ-unsaturated aldehydes (Jones and McCombie, J., 1942, 733) has been undertaken. When shaken for some hours at room temperature with, *e.g.*, 5% sulphuric acid, propenylethynylcarbinol (I) is isomerised almost quantitatively into *hex*-3-*en*-5-*yn*-2-*ol* (II) (*phenylurethane*, β-*naphthylurethane*). The constitution (II) for the latter was suggested by its much higher refractive index than that of (I), its ultra-violet absorption (see Table I and figure), and the fact that it contains two active hydrogen atoms (Zerewitinoff). Final proof was obtained by catalytic hydrogenation to methylbutylcarbinol, oxidised to methyl butyl ketone. When propenylethynylcarbinol was first prepared by Lespieau and Lombard (*Bull. Soc. chim.*, 1935, **2**, 369) by the Grignard method, it was suggested that hex-3-en-5-yn-2-ol was probably formed on decomposition of the Grignard complex with acids, since on complete hydrogenation of the product obtained in this manner they isolated a carbinol which seemed to be methylbutylcarbinol, although no proof of this identity was furnished.



On similar treatment of *iso*butenylethynylcarbinol (III) with acids, 2-*methylhex*-3-*en*-5-*yn*-2-*ol* (IV) (*phenylurethane*) is produced, absorption spectra data (Table I) and hydrogenation to dimethylbutylcarbinol (*phenylurethane*) providing proof of its constitution. 4-Methylhex-4-en-1-yn-3-ol (V) is isomerised to 3-*methylhex*-3-*en*-5-*yn*-2-*ol* (VI) (α-*naphthylurethane*) which yields 3-methylhexan-2-ol, oxidised to 3-methylhexan-2-one, on hydrogenation. 4-Ethyloct-4-en-1-yn-3-ol (VII) similarly gives 5-*ethyloct*-5-*en*-7-*yn*-4-*ol* (VIII) (α-*naphthylurethane*). These isomerised carbinols are obtained in good yields as colourless liquids which can be kept for months at 0° without undergoing appreciable decomposition or resinification.

(I.) $CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{:}CH \longrightarrow CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{:}CH$ (II.)

(III.) $CMe_2{:}CH{\cdot}CH(OH){\cdot}C{:}CH \longrightarrow CMe_2(OH){\cdot}CH{:}CH{\cdot}C{:}CH$ (IV.)

(V.) $CH_3{\cdot}CH{:}CMe{\cdot}CH(OH){\cdot}C{:}CH \longrightarrow CH_3{\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}C{:}CH$ (VI.)

(VII.) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CEt{\cdot}CH(OH){\cdot}C{:}CH \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CEt{:}CH{\cdot}C{:}CH$ (VIII.)

Hex-3-en-5-yn-2-ol (II) exhibits intense ultra-violet absorption with a maximum at 2230 A. and a marked inflexion at 2300 A. (see Fig.). The light-absorbing properties of the carbinols (IV), (VI), and (VIII) are strictly analogous both in location and in intensity of the absorption maxima (Table I) and it might well be suggested on the basis of this evidence that the conjugated vinylacetylene system resembles a conjugated diene system in light-absorption properties. The intensities of the light absorption of these vinylacetylenes are, however, markedly lower than those of typical dienes (Booker, Evans, and Gillam, *loc. cit.*) and the presence of a characteristic inflexion at about 2300 A. in the spectra of the carbinols listed in Table I renders the analogy between

* A patent application is pending involving the subject matter of this and the two following papers.

TABLE I.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{infl.}$, A.	$\epsilon_{infl.}$
Hex-3-en-5-yn-2-ol (II)	2230	13,500	2300	9,500
2-Methylhex-3-en-5-yn-2-ol (IV)	2230	10,000	2310	8,500
3-Methylhex-3-en-5-yn-2-ol (VI)	2240	13,000	2310	11,000
5-Ethyloct-5-en-7-yn-4-ol (VIII)	2270	12,500	2330	11,000
1 : 2-Dimethylvinylacetylene	2195	9,000	2260	7,000
Piperylene *	2235	23,000	—	—
$\Delta^{2:4}$-Hexadiene *	2270	22,500	—	—

* Booker, Evans, and Gillam, J., 1940, 1453.

the two chromophores rather incomplete. These inconsistencies, coupled with the fact that we find that 2 : 7-dimethylocta-3 : 5-diyn-2 : 7-diol (Zal'kind and Aĭzikovitch, *J. Gen. Chem. Russia*, 1937, **7**, 227) fails to show any high-intensity light absorption, suggest that in many respects ethylenic and acetylenic bonds are fundamentally different in their light-absorption behaviour. The acetylenic bond appears to be somewhat akin to the carbonyl bond, which, as is well known, when conjugated to an ethylenic linkage, gives rise to a maximum in the region 2200—2500 A., and, in compounds such as R·CO·CO·R, where the carbonyl groups cannot enolise, fails to produce any high-intensity absorption in the ultra-violet. Such an analogy would demand that αβ-acetylenic ketones should fail to absorb strongly in the ultra-violet, an implication which will be tested at the earliest opportunity. On the other hand, as far as can be ascertained from the literature, isolated carbonyl and acetylenic groups do not exhibit similar absorption properties, and when the latter are present in a conjugated system such as >C:CH·C:C·CH:C< the conjugation is not " crossed " as it would be by a carbonyl group similarly situated (see Parts X and XI). Further information about the rôle of acetylenic linkages in light absorption is gradually being accumulated as a result of work in this field.

Since the unisomerised ethynylcarbinols are optically transparent, measurements of ultra-violet absorption intensity can be utilised to determine the extent of isomerisation in any particular case. By employing this method, a detailed study of the kinetics of these rearrangements has been begun, but we here refer only to some experiments of a semiquantitative nature from which certain obvious conclusions can be drawn. The results recorded in Table II were obtained by treating small portions of propenylethynylcarbinol under the conditions described, isolating the product by means of ether, and determining the absorption spectrum of the residue obtained on evaporation. From the intensities observed at 2230 A. the proportion of rearranged carbinol in the product could be determined approximately.

TABLE II.

Acid reagent.	Conditions.*	Isomerisation, % (approx.).	Acid reagent.	Conditions.*	Isomerisation, % (approx.).
H_2SO_4, 10% w/v	S, 2 hrs., 20°	40	HNO_3, 1%	R, 0·5 hr., 100°	100
,, 5%	S, 12 hrs., 20°	100	H_3PO_4, 5%	S, 12 hrs., 20°	30
,, 5%	S, 2 hrs., 20°	20	,, 25%	S, 70 hrs., 20°	100
,, 2·5%	S, 48 hrs., 20°	100	H_3BO_3, 25%	R, 0·5 hr., 100°	90
,, 2·5%	S, 1 hr., 20°	5	$KHSO_4$, 10%	S, 12 hrs., 20°	60
,, 2·5%	R, 0·5 hr., 100°	100	,, 10%	S, 70 hrs., 20°	100
,, 1%	R, 0·5 hr., 100°	100	H·CO_2H, 25%	S, 12 hrs., 20°	30
,, 1%	S.d.	100	HOAc, 25%	S, 12 hrs., 20°	7
,, 0·1%	R, 0·5 hr., 100°	100	,, 25%	S, 70 hrs., 20°	30
,, 0·01%	R, 0·5 hr., 100°	40	Tartaric acid, 25%	R, 0·5 hr., 100°	100
,, 0·01%	R, 1 hr., 100°	60	Ac_2O	H, 4 hrs., 110°	0
,, 0·01%	R, 2 hrs., 100°	90		R, 4·5 hrs. in presence of anhydrous NaOAc	50
HCl, 5%	S, 12 hrs., 20°	100			

* S = Shaking, R = refluxing, S.d. = steam distillation, H = heating.

The above results demonstrate that the rate of anionotropic rearrangement of propenylethynylcarbinol is considerably accelerated by increase of temperature and also by increase in the concentration of the acid. Phenylpropenylcarbinol is smoothly isomerised in dilute acetic acid (0·5%) at the ordinary temperature (Kenyon, Partridge, and Phillips, J., 1937, 207), from which it is obvious that the mobility of the propenylethynyl system is of a comparatively low order. Dissociation-constant measurements reveal that the ethynyl group attracts electrons more strongly than the phenyl group (Ingold, *Chem. Reviews*, 1934, **15**, 239). The greater mobility of the phenylpropenyl, as compared with the propenylethynyl system is consistent with this fact, the ethynyl group being less able, because of its greater electron-attracting properties, to stabilise the positive charge on the adjacent carbon atom after the separation of the anion. However, in view of the dual influence of the phenyl group in promoting both prototropic and anionotropic changes, and other considerations, an interpretation solely in terms of the inductive effects of the groups involved must be considered insufficient. It can only be said that the phenyl group exhibits a greater resilience towards both positive and negative charges, or that it contains a more mobile electronic system, than the ethynyl group.

Burton and Ingold (J., 1928, 904) and Burton (J., 1928, 1650), who first made a systematic study of anionotropic rearrangements, mentioned that the ease of isomerisation in such systems would be expected to increase with increasing strength of the acid HX, where X is the migrating anion, *i.e.*, Br > OAc > OH. It is note-

worthy in this connection that the propenylethynyl system is stable in the presence of acetic anhydride at 110° and is isomerised only partly on heating under reflux with the same reagent, whereas Burton (J., 1929, 455) observed the complete conversion of phenylpropenylcarbinol into styrylmethylcarbinyl acetate in boiling acetic anhydride. The generalisation mentioned above is fully borne out by the observation that compounds such as propenylethynylcarbinyl chloride are so readily isomerised that their isolation is well nigh impossible (unpublished work).

In spite of treatment with 25% sulphuric acid, even at elevated temperatures, numerous attempts to isomerise vinylethynylcarbinol were unsuccessful, the starting material being recovered essentially unchanged; similarly, styrylethynylcarbinol was unaffected by shaking its ethereal solution with 10% sulphuric acid for 48 hours. The observed lack of mobility of the hydroxyl group in vinylethynylcarbinol is closely paralleled by the similar observations made by Burton and Ingold (*loc. cit.*) with phenylvinylcarbinol, the enhanced mobility in the propenylcarbinols being attributable to the greater inductive effect of the methyl group than of the hydrogen atom. This is even more readily apparent in the ease of isomerisation of *iso*butenylethynylcarbinol (see Experimental), where the still greater inductive effect of the *gem*-dimethyl group is involved. No study of the mobility of the system present in phenyl*iso*butenylcarbinol has apparently been made; this should be of interest, as this carbinol should be even more labile than the phenylpropenyl type. The presence of methyl and ethyl substituents on the carbon atom adjacent to the hydroxyl group does not appear to have any marked effect on the ease of rearrangement of 4-methylhex-4-en-1-yn-3-ol (V) and 4-ethyloct-4-en-1-yn-3-ol (VII).

The discovery of this isomerisation of unsaturated ethynylcarbinols is of considerable interest for the synthesis of polyenes related to vitamin-A, particularly in view of the recent success of Thomson and Shaw (*J. Amer. Chem. Soc.*, **1942, 64, 363**) in the selective hydrogenation of vinylacetylenes to conjugated butadienes by employing a Raney-type iron catalyst. The many implications of these rearrangements are being examined in these laboratories.

Experimental.

(M. p.'s are uncorrected. Absorption spectra were determined in alcoholic solutions. All distillations were carried out in a nitrogen atmosphere. Except where stated otherwise, light petroleum refers to that fraction of b. p. 40—60°.)

Hex-3-en-5-yn-2-ol (II).—(*a*) A mixture of propenylethynylcarbinol (220 g.) and sulphuric acid (2000 c.c.; 5% w/v) was shaken vigorously under nitrogen for 14 hours at 22°. The product was isolated by thorough extraction with ether, after saturation with salt, and the ethereal extract was washed with saturated sodium bicarbonate solution, dried, and evaporated. Two distillations of the residue yielded *hex-3-en-5-yn-2-ol* (192 g.) as a colourless oil, b. p. 103—106°/100 mm., 69—70°/18 mm., $n_D^{22°}$ 1·4791 (Found: C, 75·1; H, 8·5. C_6H_8O requires C, 75·0; H, 8·4%). On standing, the carbinol develops a brown colour and slight resinification occurs; this is appreciably retarded in the presence of a trace of quinol. *Active hydrogen* (Zerewitinoff): The carbinol (105 mg.) evolved 50·0 c.c. of methane at 758 mm. and 22°, after being heated to 90°, equivalent to 2·0 active hydrogen atoms per molecule. The *phenylurethane* separated from either aqueous alcohol or light petroleum (b. p. 60—80°) in plates, m. p. 83—84° (Found: C, 72·9; H, 6·2. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·0%). The *β-naphthylurethane* crystallised from the latter solvent in leaflets, m. p. 77—78° (Found: C, 76·8; H, 5·9. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7%).

Acetyl derivative. Hex-3-en-5-yn-2-ol (5 g.) was heated with acetic anhydride (10 g.) at 110° for 4 hours in nitrogen. Isolated in the usual manner, the *acetyl* derivative distilled as a colourless oil (6 g.) which darkened on standing; b. p. 101—103°/70 mm., $n_D^{18·5°}$ 1·4576 (Found: C, 69·35; H, 7·3. $C_8H_{10}O_2$ requires C, 69·6; H, 7·25%). *Light absorption*: Maximum, 2240 A.; log ε = 4·06.

(*b*) A mixture of propenylethynylcarbinol (20 g.) and sulphuric acid (20 c.c.; 0·1% w/v) was refluxed for 30 mins. in an atmosphere of nitrogen. Isolation of the product as described under (*a*) gave hex-3-en-5-yn-2-ol (18·4 g.), b. p. 67—70°/18 mm., $n_D^{17°}$ 1·4772.

Methylbutylcarbinol and Methyl Butyl Ketone.—A solution of hex-3-en-5-yn-2-ol (2 g.) in methyl alcohol (20 c.c.) was shaken with palladium–norit (0·5 g.; 10%) in hydrogen until absorption was complete. The catalyst was filtered off, and the solvent removed through a column; the residual methylbutylcarbinol had b. p. 135—137° (Sutter, *Helv. Chim. Acta*, 1938, **21**, 1269, gives b. p. 135—137°). A synthetic specimen of this alcohol, made by reaction between methylmagnesium iodide and *n*-valeraldehyde, had b. p. 135—137°. The carbinol was oxidised with chromic anhydride in a mixture of dilute acetic and sulphuric acids to methyl butyl ketone; semicarbazone, m. p. 121—122° (Kyner, *J. pr. Chem.*, 1901, **64**, 115, gives m. p. 122°), and 2 : 4-dinitrophenylhydrazone, m. p. 106—107° (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2957, gives m. p. 106°). Neither derivative depressed the m. p. of an authentic specimen.

2-Methylhex-3-en-5-yn-2-ol (IV).—A mixture of *iso*butenylethynylcarbinol (10 g.) and sulphuric acid (25 c.c.; 5% w/v) was shaken under nitrogen for 3 hours at 20°. Isolation in the usual manner yielded *2-methylhex-3-en-5-yn-2-ol* (7 g.), b. p. 91—93°/50 mm., $n_D^{24·5°}$ 1·4711 (Found: C, 76·1; H, 9·3. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). The *phenylurethane* separated from aqueous methyl alcohol in needles, m. p. 95—95·5° (Found: C, 73·6; H, 6·75. $C_{14}H_{15}O_2N$ requires C, 73·35; H, 6·55%).

Dimethylbutylcarbinol. 2-Methylhex-3-en-5-yn-2-ol (5 g.) in methyl alcohol (75 c.c.) was hydrogenated completely in the presence of palladium–norit (100 mg.; 10%) yielding dimethylbutylcarbinol, b. p. 85·5—88°/100 mm., $n_D^{24°}$ 1·4180 (Whitmore and Woodburn, *J. Amer. Chem. Soc.*, 1933, **55**, 363, give b. p. 139—140°/735 mm., $n_D^{20°}$ 1·4175). The *phenylurethane* formed needles from light petroleum, m. p. 44—45° (Found: N, 6·0. $C_{14}H_{21}O_2N$ requires N, 5·95%).

3-Methylhex-3-en-5-yn-2-ol (VI).—A mixture of 4-methylhex-4-en-1-yn-3-ol (10 g.) and sulphuric acid (100 c.c.; 5% w/v) was shaken under nitrogen at 20° for 21 hours. Isolation in the usual manner yielded *3-methylhex-3-en-5-yn-2-ol* (6 g.), b. p. 78—81°/20 mm. (after two distillations), $n_D^{23°}$ 1·4813 (Found: C, 76·15; H, 8·9. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). The *α-naphthylurethane* separated in needles from light petroleum (b. p. 60—80°) or aqueous methyl alcohol; m. p. 93—94° (Found: N, 5·05. $C_{18}H_{17}O_2N$ requires N, 5·0%).

3-Methylhexan-2-one. 3-Methylhex-3-en-5-yn-2-ol (13·5 g.) in ethyl acetate (100 c.c.) was hydrogenated completely in the presence of platinic oxide (0·5 g.), yielding 3-methylhexan-2-ol (9 g.), b. p. 85—87°/65 mm., $n_D^{18°}$ 1·4198. A portion of this was oxidised with chromic anhydride in dilute sulphuric acid to 3-methylhexan-2-one, b. p. 143—148°, $n_D^{20°}$ 1·4035 (Powell, Murray, and Baldwin, *J. Amer. Chem. Soc.*, 1933, **55**, 1154, give b. p. 142—145°, $n_D^{24°}$ 1·409). The semicarbazone had m. p. 112—113° (Hopff, *Ber.*, 1931, **64**, 2742, gives m. p. 114°).

5-Ethyloct-5-en-7-yn-4-ol (VIII).—A mixture of 4-ethyloct-4-en-1-yn-3-ol (30 g.) and sulphuric acid (120 c.c.; 10%

w/v) was shaken under nitrogen for 7 hours at 20°. Isolation in the usual manner yielded after two fractionations *5-ethyloct-5-en-7-yn-4-ol* (15 g.), b. p. 100—101·5°/14 mm., $n_D^{23°}$ 1·4791 (Found: C, 78·4; H, 10·5. $C_{10}H_{16}O$ requires C, 78·95; H, 10·5%). The *α-naphthylurethane* crystallised in needles from light petroleum; m. p. 75—76° (Found: C, 78·5; H, 7·25. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·15%).

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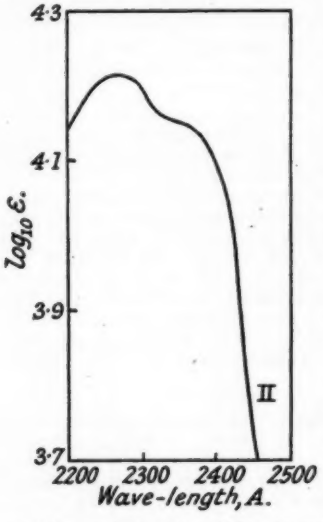
67. *Studies in the Polyene Series. Part IX. The Condensation Product of 1-Hexyne with Crotonaldehyde and its Anionotropic Rearrangement.*

By I. M. HEILBRON, E. R. H. JONES, and R. A. RAPHAEL.

Dec-2-en-5-yn-4-ol (I) is prepared from crotonaldehyde and 1-hexyne in 30% and 80% yields by the sodium in liquid ammonia and the Grignard method, respectively. It undergoes anionotropic rearrangement on treatment with 25% sulphuric acid to *dec-3-en-5-yn-2-ol* (II), which exhibits the expected high-intensity absorption in the ultra-violet, its constitution being proved by hydrogenation to methyloctylcarbinol.

IT has already been shown (Jones and McCombie, J., 1942, 733) that condensation between sodium acetylide and αβ-unsaturated aldehydes can readily be effected in liquid ammonia solution. We now find that monoalkyl acetylenes behave similarly, reaction between the sodio-compound of 1-hexyne and crotonaldehyde furnishing *dec-2-en-5-yn-4-ol* (I) (*α-naphthylurethane*) in 30% yield; the constitution of (I) was proved by hydrogenation to propylhexylcarbinol (3 : 5-*dinitrobenzoate*) and by oxidation of the latter to propyl hexyl ketone. The comparatively poor yield obtained in the above condensation is due to the reduction of 1-hexyne by sodium in liquid ammonia, an effective reducing agent for the semihydrogenation of acetylenic linkages (Campbell and Eby, *J. Amer. Chem. Soc.*, 1941, **63**, 216), although great care was taken to ensure that only the smallest excess of sodium was ever present in the ammonia solution. This was rendered difficult, however, by the extremely slow reaction of the metal with 1-hexyne, much slower than its reaction with either acetylene or vinylacetylene. The Grignard method, although unsatisfactory with acetylene itself, is more convenient with substituted acetylenes and, as was to be expected, from hexynylmagnesium bromide and crotonaldehyde, dec-2-en-5-yn-4-ol is obtained in excellent yield.



In view of the facile anionotropic rearrangement observed with propenylethynylcarbinol and similar compounds on shaking with dilute mineral acids (Part VIII, preceding paper), it was of interest to investigate the behaviour of (I) under these conditions. The substituted acetylenic group appears to have a powerful retarding influence on the ease of isomerisation, for whereas propenylethynylcarbinol is completely isomerised into hex-3-en-5-yn-2-ol on shaking with 5% sulphuric acid for 12 hours, dec-2-en-5-yn-4-ol remains unchanged even when shaken with 10% acid for 24 hours; with 25% sulphuric acid, however, it is isomerised almost quantitatively into

$CH_3 \cdot CH{:}CH \cdot CH(OH) \cdot C{:}C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ (I.)
$CH_3 \cdot CH(OH) \cdot CH{:}CH \cdot C{:}C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ (II.)

dec-3-en-5-yn-2-ol (II) (*α-naphthylurethane*). Since these experiments were not carried out in a homogeneous medium, the comparisons made above have no absolute significance, as the expected difference in water solubility between propenylethynylcarbinol and (I) may be sufficient to account for the apparent differences in ease of mobility. However, the behaviour of vinylacetylenecarbinols of similar molecular weight to (I) would appear to indicate that the solubility factor is not of great significance (see following paper); kinetic experiments in homogeneous media are in progress, and should provide an accurate picture of the effect of ethynyl substitution on the mobility of the hydroxyl group in propenylethynyl systems.

The carbinol (II) exhibits intense light absorption in the ultra-violet (see figure), exactly analogous in both location and intensity to that observed with the conjugated vinylacetylene carbinols (Part VIII). It is noteworthy that complete substitution in the acetylenic group has little or no effect on either the location or the intensity of the maximum absorption, and the characteristic inflexion already noted is again apparent. The constitution of (II) is proved by its hydrogenation to methyloctylcarbinol (3 : 5-*dinitrobenzoate*), and oxidation of the latter to methyl octyl ketone.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

Dec-2-en-5-yn-4-ol (I).—(*a*) 1-Hexyne (60 g.) and sodium (16·7 g.) were added to liquid ammonia (1500 c.c.) in such a manner that the blue colour persisted for the shortest possible time. When the addition was complete, the mixture was treated dropwise with crotonaldehyde (50 g.) in ether (100 c.c.), and stirring and cooling were continued for a further

2 hours, after which ammonium chloride (40 g.) was added and the ammonia was allowed to evaporate off overnight. The product was isolated by means of ether, and two distillations gave *dec-2-en-5-yn-4-ol* (33 g.) as a colourless liquid, b. p. 90°/1 mm., $n_D^{21°}$ 1·4681 (Found: C, 78·3; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff): the carbinol (178 mg.) gave 26·3 c.c. of methane at 22·5°/775 mm., corresponding to 1·05 active hydrogen atoms per molecule. It exhibits no absorption of appreciable intensity in the range 2200—4000 A. The *α-naphthylurethane*, prepared in the usual manner, crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 69° (Found: N, 4·1. $C_{21}H_{23}O_2N$ requires N, 4·35%).

(*b*) After a solution of 1-hexyne (12 g.) in ether (20 c.c.) had been added dropwise to an ethereal solution of ethylmagnesium bromide (from 3 g. of magnesium), the mixture was refluxed for 3 hours, cooled, treated during 1½ hours with a solution of crotonaldehyde (8·9 g.) in ether (20 c.c.), and set aside overnight. The Grignard complex was decomposed with ammonium nitrate (30 g.) in water (50 c.c.), and from the ethereal solution were isolated 15 g. of dec-2-en-5-yn-4-ol, b. p. 83—85°/1 mm., $n_D^{18°}$ 1·4700.

Propylhexylcarbinol and Propyl Hexyl Ketone.—A solution of dec-2-en-5-yn-4-ol (9·2 g.) in methyl alcohol (150 c.c.) was shaken with hydrogen in the presence of palladium–norit (100 mg.; 10%) until absorption was complete. The catalyst was filtered off, but although the solvent was distilled slowly through a column, considerable volatilisation of the product occurred (we have since found that methyl and ethyl acetates are ideal solvents for this type of hydrogenation). Distillation of the residual oil gave propylhexylcarbinol (2·5 g.), b. p. 71°/1 mm., $n_D^{21°}$ 1·4312 (Karrer, Shibata, Wettstein, and Jacubowicz, *Helv. Chim. Acta*, 1930, **13**, 1300, give b. p. 206—207°/724 mm.). The 3 : 5-*dinitrobenzoate* crystallised in needles, m. p. 24°, from light petroleum (b. p. 40—60°) (Found: N, 8·3. $C_{17}H_{24}O_6N_2$ requires N, 7·95%). Oxidation of the carbinol with chromic acid in the usual manner gave propyl hexyl ketone, b. p. 84°/3 mm., $n_D^{21°}$ 1·4240, which gave a semicarbazone, m. p. 56° (or as low as 51°, depending upon the rate of heating) (Karrer *et al.*, *loc. cit.*, give m. p. 51—52°).

Dec-3-en-5-yn-2-ol (II).—A mixture of dec-2-en-5-yn-4-ol (10 g.) and sulphuric acid (100 c.c.; 25% w/v) was shaken for 24 hours at 20° under nitrogen. Isolation by means of ether yielded *dec-3-en-5-yn-2-ol* (8 g.), b. p. 113—114°/3 mm., $n_D^{22°}$ 1·4833 (Found: C, 78·5; H, 10·4. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff): the carbinol (177 mg.) gave 26·5 c.c. of methane at 18°/765 mm., corresponding to 0·95 active hydrogen atom per molecule. *Light absorption* (see fig.): Maximum, 2260 A., log ϵ = 4·21; inflexion, 2350 A.; log ϵ = 4·18. The *α-naphthylurethane* formed needles from light petroleum (b. p. 40—60°), m. p. 65° (Found: N, 4·45. $C_{21}H_{23}O_2N$ requires N, 4·35%).

Methyloctylcarbinol and Methyl Octyl Ketone.—A solution of dec-3-en-5-yn-2-ol (5 g.) in ether (150 c.c.) was shaken with hydrogen in the presence of palladium–norit (100 mg.; 10%) until absorption was complete. The catalyst was removed, and evaporation of the ether through a column gave methyloctylcarbinol (4·5 g.), b. p. 209°, $n_D^{19°}$ 1·4342 (Pickard and Kenyon, J., 1911, **99**, 58, give b. p. 210—211°). The 3 : 5-*dinitrobenzoate* separated from light petroleum (b. p. 40—60°) in clusters of needles, m. p. 44° (Found: N, 8·1. $C_{17}H_{24}O_6N_2$ requires N, 7·95%). Oxidation of the carbinol with chromic acid gave methyl octyl ketone, b. p. 86°/3 mm., $n_D^{21°}$ 1·4230 (Rupe and Willi, *Helv. Chim. Acta*, 1932, **15**, 845, give b. p. 92°/10 mm., $n_D^{25°}$ 1·4263). The semicarbazone formed plates from methyl alcohol, m. p. 124° (Rupe and Willi, *loc. cit.*, give m. p. 126°).

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68. *Studies in the Polyene Series. Part X. Condensation of 3-Methylpent-2-en-4-yne (1 : 2-Dimethylvinylacetylene) with Butaldehyde, Crotonaldehyde, and Citral. Anionotropic Rearrangements with Vinylacetylenecarbinols derived from αβ-Unsaturated Aldehydes.*

By I. M. HEILBRON, A. W. JOHNSON, E. R. H. JONES, and R. A. RAPHAEL.

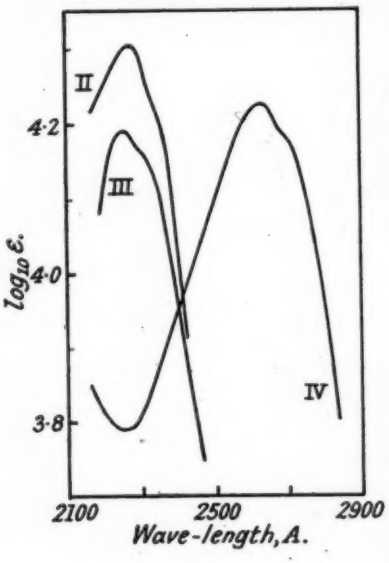
3-Methylpent-2-en-4-yne condenses normally with the above aldehydes by the Grignard method, and the sodium in liquid ammonia process is shown to be applicable in the one case in which it is employed. *7-Methylnonan-4-ol* is obtained by hydrogenation of both the butaldehyde and the crotonaldehyde product, and the latter smoothly undergoes the expected anionotropic conversion into the isomeric *divinylacetylenecarbinol* (IV) on treatment with dilute acid. The carbinol (VI) from citral is extremely labile, undergoing simultaneous rearrangement and dehydration, even on distillation at 10^{-4} mm.

ETHYNYLCARBINOLS from αβ-unsaturated aldehydes have been prepared by condensation with sodium acetylide in liquid ammonia (Jones and McCombie, J., 1942, 733), and their rearrangement in the presence of acidic reagents has been investigated (*idem*, this vol., p. 261). In Part IX (previous paper) the condensation of 1-hexyne with crotonaldehyde and isomerisation of the acetylenic carbinol with sulphuric acid was described, so a study of the reaction of conjugated vinylacetylenes with αβ-unsaturated aldehydes represents a logical continuation of this programme, directed ultimately towards the synthesis of polyene alcohols related to vitamin A. Many condensations between conjugated vinylacetylenes containing a free ethynyl group and carbonyl compounds are recorded in the literature, but there are few examples of reactions of vinylacetylene and its homologues with unsaturated aldehydes. Carothers and Jacobson (*J. Amer. Chem. Soc.*, 1933, **55**, 1097) reported that condensation between vinylacetylene and crotonaldehyde gave rise to resinous products and Nazarov and Elizarova (*Chem. Abstracts*, 1942, **36**, 742) claimed that, although the condensation of vinylacetylenemagnesium bromide and furfuraldehyde gave the desired carbinol, it darkened rapidly during isolation and exploded on attempted distillation.

It is generally agreed that the most satisfactory method of condensing conjugated vinylacetylenes with aldehydes and ketones is by means of their Grignard compounds, although other condensing agents (*e.g.*, sodamide, potassium hydroxide, and potassium *tert.*-amyloxide) have been employed (Carothers *et al.*, *J.*

Amer. Chem. Soc., **1933**, **55**, 1094, 1097; F.P., 753,465; U.S.P. 1,963,934—5; Nazarov *et al.*, *Chem. Abstracts*, **1939**, **33**, 5682; **1941**, **35**, 4733, 5092; **1942**, **36**, 1296; Thompson, Milas, and Rovno, *J. Amer. Chem. Soc.*, **1941**, **63**, 752). As far as we are aware, no syntheses of vinylacetylene-carbinols have been made from the sodium derivatives of the hydrocarbons in liquid ammonia solution.

FIG. 1.



As a necessary preliminary to the employment of crotonaldehyde in these reactions, the Grignard condensation between butaldehyde and 3-methylpent-2-en-4-yne (I) was examined. This furnished a 60% yield of *7-methylnon-7-en-5-yn-4-ol* (II) (*3 : 5-dinitrobenzoate* and *β-naphthylurethane*) which on hydrogenation gave *7-methylnonan-4-ol* (*3 : 5-dinitrobenzoate*), oxidised to *7-methylnonan-4-one* (*phenylsemicarbazone*). The carbinol (II) exhibited light absorption (Fig. 1 and table) similar to that

(I.) $HC{:}C\cdot CMe{:}CHMe$
(II.) $CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot C{:}C\cdot CMe{:}CHMe$
(III.) $CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{:}C\cdot CMe{:}CHMe$
(IV.) $CH_3\cdot CH(OH)\cdot CH{:}CH\cdot C{:}C\cdot CMe{:}CHMe$
(V.) $CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{:}C\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$

previously recorded (Jones and McCombie, this vol., p. 261) for compounds containing the conjugated vinylacetylene chromophore. With crotonaldehyde and dimethylvinylacetylene, *7-methylnona-2 : 7-dien-5-yn-4-ol* (III) (*α-naphthylurethane*) was obtained by either the Grignard (80% yield) or the sodium in liquid ammonia (65%) method. The anticipated absorption spectrum (Fig. 1 and table) was observed, and complete hydrogenation of (III) gave 7-methylnonan-4-ol, identical with that given by the butaldehyde product (II).

	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{infl.}$, A.	$\epsilon_{infl.}$
3-Methylpent-2-en-4-yne (I)	2195	9,000	2260	7,000
7-Methylnon-7-en-5-yn-4-ol (II) (Fig. 1)	2280	20,500	2320	18,000
7-Methylnona-2 : 7-dien-5-yn-4-ol (III) (Fig. 1)	2250	15,500	2290	15,000
Hex-3-en-5-yn-2-ol (Part VIII)	2230	13,000	2300	9,500
Dec-3-en-5-yn-2-ol (Part IX)	2260	16,000	2350	15,000
7-Methylnona-3 : 7-dien-5-yn-2-ol (IV) (Fig. 1)	2640	16,500	2690	15,500
Octatrienol	2760	46,500	—	—
	2645	53,000	—	—
	2560	42,500	—	—

On being shaken for 24 hours with 5% sulphuric acid, the carbinol (III) was converted in good yield into the isomeric *7-methylnona-3 : 7-dien-5-yn-2-ol* (IV) (*α-naphthylurethane*). Hydrogenation of (IV) yielded *7-methylnonan-2-ol* (*3 : 5-dinitrobenzoate*) which was oxidised to *7-methylnonan-2-one* (*semicarbazone, phenylsemicarbazone*). The comparative ease of isomerisation of (III) is in striking contrast to that of the isomeric dec-2-en-5-yn-4-ol (V) (preceding paper) which required 25% acid for complete conversion.

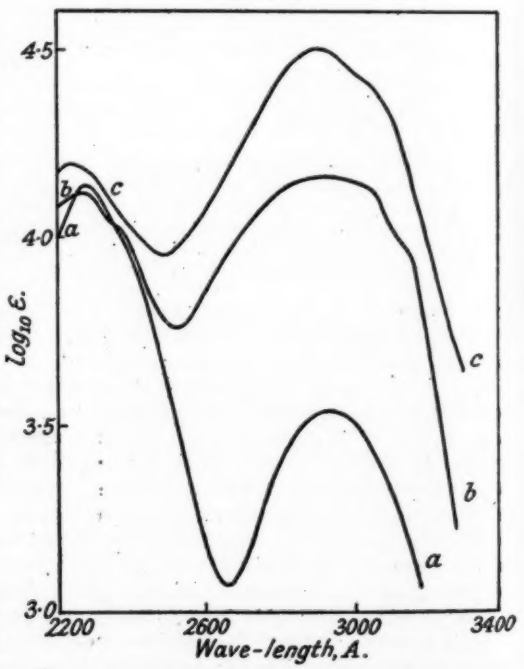
The absorption spectrum of (IV) (Fig. 1 and table) reveals that the *s*-divinylacetylene chromophore absorbs at corresponding wave-lengths to a conjugated triene, although an appreciable difference in intensity is observed, similar to the differences already noted with the conjugated vinylacetylenes (Part VIII).

When citral is condensed with 3-methylpent-2-en-4-yne (I) by the Grignard method, the undistilled product consists mainly of the carbinol (VI) as shown by the fact that it contains 0·9 active hydrogen atom and also by its absorption spectrum [Fig. 2(*a*)], which, with its maximum at 2250 A., is

$Me_2C{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH(OH)\cdot C{:}C\cdot CMe{:}CHMe$ (VI.)
$Me_2C{:}CH\cdot CH_2\cdot CH_2\cdot C(OH)Me\cdot CH{:}CH\cdot C{:}C\cdot CMe{:}CHMe$ (VII.)
$Me_2C{:}CH\cdot CH_2\cdot CH{:}CMe\cdot CH{:}CH\cdot C{:}C\cdot CMe{:}CHMe$ (VIII.)

similar to those of the carbinols (II) and (III). On attempting to purify (VI) by distillation at 10^{-4} mm., considerable rearrangement occurs [Fig. 2(*b*)], accompanied by dehydration, affording the hydrocarbon (VIII)—the intermediate tertiary carbinol (VII), which would be expected to

FIG. 2.



absorb at about 2650 A. by analogy with (IV), evidently undergoes instantaneous dehydration. The conversion of (VI) into (VIII) could not be made complete, however, distillation of (VI) at 10^{-2} mm., followed by persistent chromatographic purification, yielding a product [light absorption, Fig. 2(*c*)] which still contained a few units % of carbinol. Complete hydrogenation of this material, followed by distillation from sodium, gave a saturated hydrocarbon, presumably 2 : 6 : 11-*trimethyl*-n-*tridecane*.

Experimental.

7-Methylnon-7-en-5-yn-4-ol (II).—3-Methylpent-2-en-4-yne (31 g.; Thompson, Burr, and Shaw, *J. Amer. Chem. Soc.*, 1941, **63**, 188) in ether (70 c.c.) was gradually added to a solution of ethylmagnesium bromide (from 9·2 g. of magnesium) in ether (100 c.c.) during an hour, after which the reaction mixture was refluxed for 2 hours. It was then cooled, treated dropwise with butaldehyde (27·4 g.) in ether (100 c.c.), set aside overnight, and the Grignard complex decomposed with ammonium chloride solution (ice). Isolated from the ethereal phase in the usual way, *7-methylnon-7-en-5-yn-4-ol* (37 g.) was obtained as a colourless mobile liquid, b. p. 106°/15 mm., $n_D^{18°}$ 1·4800 (Found : C, 79·3; H, 10·8. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff) : The carbinol (250 mg.) evolved 41·4 c.c. of methane at 20°/773 mm., equivalent to 1·0 active hydrogen atom. The 3 : 5-*dinitrobenzoate* formed needles from alcohol, m. p. 53° (Found : C, 59·1; H, 5·2; N, 8·3. $C_{17}H_{18}O_6N_2$ requires C, 58·95; H, 5·2; N, 8·1%). The *β-naphthylurethane* crystallised from aqueous alcohol in plates, m. p. 46° (Found : C, 78·5; H, 7·4. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·2%).

7-Methylnonan-4-ol.—A solution of the above carbinol (4·3 g.) in methyl alcohol (200 c.c.) was shaken with hydrogen in the presence of platinic oxide (0·1 g.) until absorption was complete. The catalyst and solvent were removed, yielding *7-methylnonan-4-ol* as a pleasant-smelling oil, b. p. 94°/12 mm., $n_D^{22°}$ 1·4317 (Found : C, 76·1; H, 13·4. $C_{10}H_{22}O$ requires C, 76·0; H, 13·9%). The 3 : 5-*dinitrobenzoate* crystallised from aqueous alcohol in needles, m. p. 60° (Found : C, 58·0; H, 6·8; N, 8·0. $C_{17}H_{24}O_6N_2$ requires C, 57·95; H, 6·85; N, 7·95%).

7-Methylnonan-4-one.—Oxidation of the above carbinol with chromic acid yielded *7-methylnonan-4-one* as a pleasant-smelling oil, b. p. 86°/11 mm., $n_D^{22°}$ 1·4246 (Found : C, 76·7; H, 13·1. $C_{10}H_{20}O$ requires C, 76·85; H, 12·9%). The *phenylsemicarbazone* separated from aqueous methyl alcohol in needles, m. p. 65° (Found : N, 14·25. $C_{17}H_{27}ON_3$ requires N, 14·5%)

7-Methylnona-2 : 7-dien-5-yn-4-ol (III).—(*a*) 3-Methylpent-2-en-4-yne (40 g.) and sodium (13 g.) were added to liquid ammonia (1000 c.c.) at such a rate that no appreciable excess of sodium was ever present in solution. Crotonaldehyde (35 g.) in ether (50 c.c.) was then added, and stirring and cooling were continued for a further 2 hours; the mixture was then treated with ether (200 c.c.) and ammonium chloride (35 g.), and the ammonia allowed to evaporate off overnight in a slow stream of nitrogen. The reaction product was isolated by steam distillation and extraction with ether, yielding *7-methylnona-2 : 7-dien-5-yn-4-ol* (49 g.) as a colourless liquid, b. p. 127°/16 mm., 85°/0·5 mm., $n_D^{22°}$ 1·4963 (Found : C, 79·8; H, 9·6. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%). *Active hydrogen* (Zerewitinoff) : The carbinol (114 mg.) gave 32·4 c.c. of methane at 21°/756 mm., corresponding to 1·0 active hydrogen atom per molecule. *Semimicrohydrogenation :* A mixture of the carbinol (132 mg.) and palladium–norit (50 mg.) in methyl alcohol absorbed 68·4 c.c. of hydrogen at 21°/748 mm., equivalent to $|\overline{\overline{4}}0$. The *α-naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in small needles, m. p. 98° (Found : N, 4·45. $C_{21}H_{21}O_2N$ requires N, 4·4%).

(*b*) A solution of 3-methylpent-2-en-4-yne (20 g.) in dry ether (25 c.c.) was slowly added to an ethereal solution of ethylmagnesium bromide (from 6 g. of magnesium), and the mixture refluxed for 2 hours. The cooled solution was treated dropwise with crotonaldehyde (18 g.) in ether (25 c.c.) and set aside overnight. Decomposition of the Grignard complex with ammonium nitrate (60 g.) and water (100 c.c.) and isolation from the ethereal solution gave 7-methylnona-2 : 7-dien-5-yn-4-ol (31 g.), b. p. 86—88°/1 mm., $n_D^{20°}$ 1·4970.

7-Methylnona-3 : 7-dien-5-yn-2-ol (IV).—A mixture of 7-methylnona-2 : 7-dien-5-yn-4-ol (20 g.) and sulphuric acid (200 c.c.; 5% w/v) was shaken under nitrogen at 20° for 24 hours. Isolation of the product in the usual manner gave *7-methylnona-3 : 7-dien-5-yn-2-ol* (17·5 g.), b. p. 122°/16 mm., 81—82°/1 mm., $n_D^{21°}$ 1·5210 (Found : C, 80·1; H, 9·5. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%). *Active hydrogen* (Zerewitinoff) : The carbinol (125 mg.) evolved 38·2 c.c. of methane at 23°/763 mm., corresponding to 0·95 active hydrogen atom per molecule. *Semimicrohydrogenation :* A mixture of the carbinol (151 mg.) and palladium–norit (50 mg.) in methyl alcohol absorbed 97·8 c.c. of hydrogen at 23°/755 mm., equivalent to $|\overline{\overline{3·95}}$. The *α-naphthylurethane* crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 82° (Found : N, 4·55. $C_{21}H_{21}O_2N$ requires N, 4·4%).

7-Methylnonan-2-ol.—A solution of the above carbinol (10 g.) in acetic acid (100 c.c.) was shaken with hydrogen in the presence of platinic oxide (100 mg.) until absorption was complete. The filtered solution was neutralised with sodium hydroxide and thoroughly extracted with ether, from which was isolated *7-methylnonan-2-ol*, an oil with a pleasant odour, b. p. 93°/4 mm., $n_D^{18°}$ 1·4330 (Found : C, 76·0, 77·9; H, 13·0, 14·0. $C_{10}H_{22}O$ requires C, 76·0; H, 13·9%). The 3 : 5-*dinitrobenzoate* crystallised from aqueous alcohol in needles, m. p. 65° (Found : N, 7·6. $C_{17}H_{24}O_6N_2$ requires N, 7·95%).

7-Methylnonan-2-one.—Oxidation of 7-methylnonan-2-ol with chromic acid gave *7-methylnonan-2-one* as a pleasant-smelling liquid, b. p. 116°/6 mm., $n_D^{22°}$ 1·4257. For analysis the ketone was regenerated from the semicarbazone by steam-distillation with phthalic anhydride (Found : C, 76·2; H, 12·7. $C_{10}H_{20}O$ requires C, 76·85; H, 12·9%). The *semicarbazone* formed plates from aqueous methyl alcohol, m. p. 124° (Found : N, 19·3. $C_{11}H_{23}ON_3$ requires N, 19·7%). The *phenylsemicarbazone* crystallised from aqueous methyl alcohol in needles, m. p. 95·5° (Found : N, 14·1. $C_{17}H_{27}ON_3$ requires N, 14·5%).

Condensation of Citral with 3-Methylpent-2-en-4-yne.—A solution of 3-methylpent-2-en-4-yne (14·7 g.) in ether (50 c.c.) was treated with an ethereal solution of ethylmagnesium bromide (from 4·3 g. of magnesium), the mixture was refluxed for 2 hours, cooled, treated dropwise (1 hour) with a solution of citral (27·4 g.) in ether (100 c.c.), and set aside overnight. After 1 hour's refluxing, the Grignard complex was decomposed in the usual manner, and the ethereal solution yielded the carbinol (30·5 g.) as a dark oil, $n_D^{25°}$ 1·5040. *Active hydrogen* (Zerewitinoff) : The product (156 mg.) evolved 14·3 c.c. of methane at 24°/768 mm., equivalent to 0·9 active hydrogen atom per molecule. *Light absorption :* Maxima, 2250 and 2920 A.; $E^{1\%}_{1\text{ cm.}}$, 610 and 160, respectively. Distillation of a portion of the product at 70- -80° (bath temp.)/10^{-4} mm. gave a pale yellow oil, $n_D^{24°}$ 1·5298, with maxima at 2250 and 2930 A.; $E^{1\%}_{1\text{ cm.}}$, 530 and 620, respectively. The main product underwent further dehydration on distillation at 10^{-2} mm., b. p. 114—116°, $n_D^{22°}$ 1·5349, and this was purified by chromatographic analysis on alumina from light petroleum (b. p. 40—60°), yielding the slightly impure hydrocarbon as a colourless oil, rapidly becoming yellow in air, $n_D^{21°}$ 1·5628 (Found : C, 87·5; H, 9·9. $C_{16}H_{22}$ requires C, 89·65; H, 10·35%). *Active hydrogen* (Zerewitinoff) : The product (142 mg.) evolved 1·3 c.c. of methane at 21°/762 mm. *Light absorption :* Maxima, 2250 and 2920 A.; $E^{1\%}_{1\text{ cm.}}$, 570 and 1320, respectively.

2 : 6 : 11-*Trimethyl*-n-*tridecane.*—A solution of the above slightly impure carbinol (5·1 g.) in methyl alcohol (250 c.c.) was shaken with hydrogen in the presence of platinic oxide (0·1 g.) until absorption was complete. After removal of

catalyst and solvent, the product was set aside over sodium for several days, and distillation from sodium then gave 2 : 6 : 11-*trimethyl*-n-*tridecane*, b. p. 152°/16 mm., $n_D^{20°}$ 1·4375 (Found: C, 85·0; H, 14·8. $C_{16}H_{34}$ requires C, 84·85; H, 15·15%).

The authors are indebted to the Rockefeller Foundation and to I.C.I. (Dyestuffs) Ltd. for financial assistance. They also wish to thank Mr. M. B. Green for assistance with the crotonaldehyde–dimethylvinylacetylene condensation.

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69. *Studies in the Polyene Series. Part XI. The Anionotropic Rearrangement of the Acetylenic Glycol from Crotonaldehyde.*

By I. M. HEILBRON, E. R. H. JONES, and R. A. RAPHAEL.

Treatment of an ethereal solution of the acetylenic glycol (I) from crotonaldehyde with 10% sulphuric acid brings about a dual anionotropic rearrangement resulting in the formation of the isomeric *glycol* (II). The constitution of the latter is established by hydrogenation to *decane*-2 : 9-*diol* and subsequent oxidation to suberic acid. The light absorption of (II) is consistent with the presence of the conjugation dienyne chromophore in the molecule.

THE preparation and properties of the symmetrical acetylenic glycols derived from saturated aldehydes and ketones have been extensively investigated, particularly by Dupont (*Ann. Chim.*, 1913, **30**, 485), following Iotsitch (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 239; 1903, **35**, 430, 1269; 1906, **38**, 252, 656). Both investigators utilised acetylenedimagnesium bromide, and this remains the most convenient laboratory method (see *inter alia*, Zalkind and Labuzov, *J. Gen. Chem. Russia*, 1939, **9**, 1525; Marvel and Dunlap, *J. Amer. Chem. Soc.*, 1939, **61**, 2716; Schokina, Kildischeva, and Preobashenski, *J. Gen. Chem. Russia*, 1941, **11**, 425). Glycol formation can also be effected by direct interaction of acetylene and carbonyl compounds, catalysts such as potassium hydroxide (Babajan, *ibid.*, 1940, **10**, 480, 1177) or heavy-metal acetylides (I.G. Farbenind., B.P. 508,062; General Aniline and Film Corp., U.S.P. 2,238,471) being used. Both symmetrical and unsymmetrical glycols can be made by condensing ethynylcarbinols with carbonyl compounds, and although the Grignard method has been mainly employed for this purpose (see *inter alia*, Marvel, Mozingo, and Kirkpatrick, *J. Amer. Chem. Soc.*, 1939, **61**, 2006; Marvel and Walton, *J. Org. Chem.*, 1942, **7**, 93; Zalkind and Gverdtsiteli, *J. Gen. Chem. Russia*, 1939, **9**, 855), condensing agents such as sodamide (Henecka, *Chem. Abstracts*, 1937, **31**, 2592; Burkhardt and Hindley, J., 1938, 987), potassium *tert.*-butoxide (*idem, ibid.*), and potassium hydroxide (Babajan, *loc. cit.*, p. 1177) are also effective. A process is also described (McCallum, U.S.P. 2,162,676) whereby an alkali- or alkaline-earth-metal compound of an ethynylcarbinol is heated to 60°, whereupon the metal compound of the corresponding acetylenic glycol is produced in good yield.

The acetylenic glycol from crotonaldehyde (deca-2 : 8-dien-5-yn-4 : 7-diol) (I) was prepared originally by Dupont (*loc. cit.*) by the Grignard method; the only other mention in the literature is its formation, in unstated yield, by the interaction of crotonaldehyde with acetylene in the presence of copper acetylide at 120—130° (I.G. Farbenind., *loc. cit.*). We have found Dupont's method satisfactory, although the yield of the pure crystalline product is not above 50%. The glycol can also be obtained, in somewhat poorer yield, by condensation of the Grignard complex from propenylethynylcarbinol with crotonaldehyde (unpublished work), but all attempts to prepare it by condensation of crotonaldehyde either with acetylene itself or with propenylethynylcarbinol by means of sodium in liquid ammonia have proved fruitless. The use of the other condensing agents described above is ruled out because of their powerful catalytic effect on the self-condensation of crotonaldehyde.

An investigation of the behaviour of the glycol (I) in the presence of acidic reagents has now been undertaken, since the corresponding ethynylcarbinol undergoes a facile anionotropic rearrangement under these conditions (Jones and McCombie, Part VIII, this vol., p. 261). On shaking an ethereal solution of

(I.) $CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH_3$ $CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CMe{:}CH{\cdot}CH_3$

(II.) $CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_3$ (III.)

the glycol (I) with 10% sulphuric acid, an isomeric glycol, produced almost quantitatively, was isolated as a viscous liquid (*bisphenylurethane*, m. p. 181°). Proof of its constitution as *deca*-3 : 7-*dien*-5-*yn*-2 : 9-*diol* (II) was readily obtained by hydrogenation to *decane*-2 : 9-*diol*, m. p. 33° (*bisphenylurethane*) which was oxidised to the known decane-2 : 9-dione (*dioxime*), which in turn was oxidised to suberic acid with hypobromite.

Since the unisomerised material (I) is a crystalline solid, m. p. 91°, it is probably stereochemically pure, being either the *meso*- or racemic form, presumably of the *trans-trans*-glycol. The liquid isomer (II) is certainly a mixture of at least two stereoisomeric forms, for on one occasion a small quantity of a solid glycol was isolated after long standing.

Further evidence of the correctness of the structure assigned to (II) is provided by its absorption spectrum (Fig. 1 and table) and that of its *diacetate* (Fig. 2 and table), both of which closely resemble those of 7-methylnona-3 : 7-dien-5-yn-2-ol (III) (Heilbron, Johnson, Jones, and Raphael, preceding paper) and octatrienol in

the location of the maxima. As was to be expected from previous observations, the intensity of the absorption of the conjugated dienyne systems is much less than that of the conjugated trienol.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$
Deca-3 : 7-dien-5-yn-2 : 9-diol (II) (Fig. 1)	—	—	2650	21,500	2800	19,000
Diacetate of (II) (Fig. 2)	2560	14,000	2650	22,000	2780	18,500
7-Methylnona-3 : 7-dien-5-yn-2-ol (III)	—	—	2640	16,500	—	—
Octatrienol	2560	42,500	2645	53,000	2780	46,500

FIG. 1.

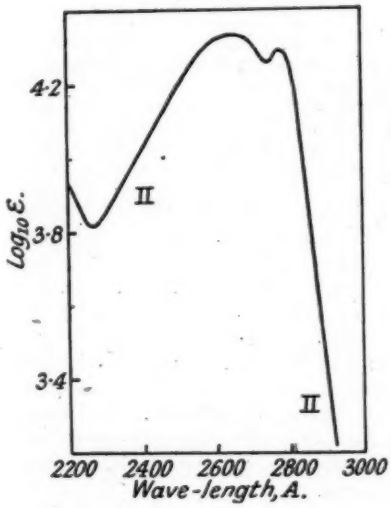
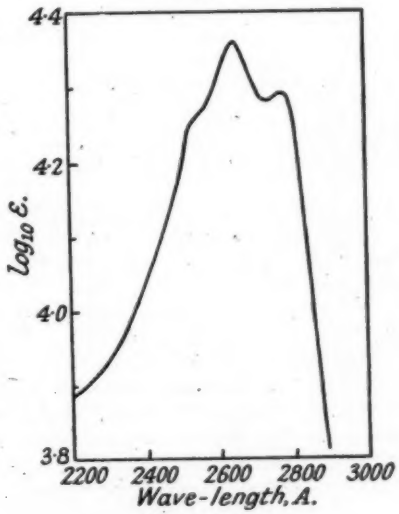


FIG. 2.



Diacetate of II.

We believe the dual anionotropic rearrangement described here to be unique, and we are exploring the scope of this novel reaction.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

Deca-2 : 8-dien-5-yn-4 : 7-diol (I) (cf. *Dupont, loc. cit.*).—Pure, dry acetylene was passed into a solution of ethylmagnesium bromide (from magnesium, 12 g.) in ether (100 c.c.) during 24 hours, the volume of the solution being maintained constant by continuous addition of ether. Freshly distilled crotonaldehyde (35 g.) was then added during 1 hour with vigorous stirring which was continued for a further 2 hours, after which the Grignard complex was decomposed with a saturated solution of ammonium chloride (60 g.). The aqueous layer was repeatedly extracted with ether and the combined extracts were washed with dilute sulphuric acid and sodium bicarbonate solution and dried. Evaporation of the ether gave a brown, viscous liquid (30 g.), which solidified almost completely on standing at 0°. The crystalline glycol was freed from oily contaminants by trituration with a small quantity of ether at 0°, and then separated from carbon tetrachloride or light petroleum (b. p. 80—100°) in prisms (28 g.), m. p. 91° (Dupont, *loc. cit.*, gives m. p. 90—92°). Small quantities of the crude glycol have been distilled at 70—75° (bath temp.)/10^{-4} mm. but this effects little purification: distillation of large amounts may result in explosive decomposition. The glycol shows no appreciable light absorption in the range 2200—4000 A.

Deca-3 : 7-dien-5-yn-2 : 9-diol (II).—A solution of the above glycol (5 g.) in ether (20 c.c.) was shaken at 20° under nitrogen with sulphuric acid (30 c.c., 10% w/v) for 24 hours, and from the washed and dried ethereal phase there were obtained 4·3 g. of *deca-3 : 7-dien-5-yn-2 : 9-diol*, a viscous liquid, b. p. 65—70° (bath temp.)/10^{-4} mm., $n_D^{21°}$ 1·5511 (Found: C, 72·5; H, 8·5. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%). On one occasion, after standing for many weeks at 0°, a small sample was obtained as needles, m. p. 56·5—57°, presumably a pure isomer. *Active hydrogen* (Zerewitinoff): The glycol (78 mg.) evolved 22·8 c.c. of methane at 22°/762 mm., equivalent to 1·9 active hydrogen atoms per molecule. The *diacetate*, prepared by the action of acetyl chloride on a pyridine solution of the glycol, was obtained as a comparatively mobile liquid, which darkened somewhat on standing; b. p. 131—132°/10^{-3} mm., $n_D^{22°}$ 1·5005 (Found: C, 67·3; H, 7·25. $C_{14}H_{18}O_4$ requires C, 67·15; H, 7·25%). The *bisphenylurethane* crystallised from ethyl acetate in needles, m. p. 181° (Found: N, 7·1. $C_{24}H_{24}O_4N_2$ requires N, 6·9%).

Decane-2 : 9-diol.—A solution of deca-3 : 7-dien-5-yn-2 : 9-diol (5 g.) in methyl alcohol (30 c.c.) was shaken with hydrogen in the presence of platinic oxide (10 mg.) until absorption was complete. Removal of the catalyst and solvent gave *decane-2 : 9-diol* (4·6 g.) as a viscous liquid, b. p. 114°/5 mm., $n_D^{21·5°}$ 1·4505, which on standing slowly formed large prisms, m. p. 33° (Found: C, 68·85; H, 12·35. $C_{10}H_{22}O_2$ requires C, 68·9; H, 12·7%). *Active hydrogen* (Zerewitinoff): The glycol (53 mg.) evolved 15·3 c.c. of methane at 24°/756 mm., corresponding to 2·1 active hydrogen atoms per molecule. The *diacetate* was obtained as a mobile liquid, b. p. 108°/4 mm., $n_D^{25°}$ 1·4281 (Found: C, 64·7; H, 10·3. $C_{14}H_{26}O_4$ requires C, 65·1; H, 10·15%). The *bisphenylurethane* crystallised from methyl alcohol in plates, m. p. 134° (Found: C, 69·9; H, 7·8. $C_{24}H_{32}O_4N_2$ requires C, 69·85; H, 7·8%).

Decane-2 : 9-dione.—This was obtained in 65% yield by oxidation of the diol (2 g.) with chromic anhydride in sulphuric acid. On crystallisation from light petroleum (b. p. 40—60°), it formed leaflets, m. p. 62° (Blaise and Koehler, *Bull. Soc. chim.*, 1909, **5**, 691 gave m. p. 64°). The *dioxime* separated from benzene as a microcrystalline powder, m. p. 132° (Found: N, 14·3. $C_{10}H_{20}O_2N_2$ requires N, 14·0%).

Suberic acid. Decane-2 : 9-dione (100 mg.) was shaken with sodium hypobromite solution (10 c.c.; 15%) for 48 hours

at 20°. The acid product, isolated from the acidified reaction mixture by means of ether, on crystallisation from water gave suberic acid, m. p. 136°, and 138° when mixed with an authentic specimen (m. p. 139°). Oxidation of the dione with nitric acid gave adipic acid.

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70. *The Dissociation Constants of Some Acids in Mixed Solvents.*

By J. C. SPEAKMAN.

Thermodynamic dissociation constants (K_1 and K_2) of some dibasic acids in aqueous alcohol and aqueous dioxan have been determined by using the glass electrode in conjunction with a cell involving liquid–liquid potentials. Similar measurements have been made with benzoic acid, and the dissociation constants of this acid have also been found from measurements on cells not involving liquid junctions. The significance of results for mixed solvents obtained by the former method is considered. The dependence of K_1/K_2 for a dibasic acid upon the structure of the molecule and the composition of the solvent is discussed.

DIFFICULTIES besetting the definition of the pH scale in general, and in particular the determination of the dissociation constant of an acid from the E.M.F. of a cell involving liquid junctions, are enhanced when an attempt is made to compare dissociation constants in different solvents (*e.g.*, Michaelis and Mizutani, *Z. physikal. Chem.*, 1925, **116**, 135; Brönsted, *Chem. Reviews*, 1928, **5**, 291; Wynne-Jones, *Proc. Roy. Soc.*, 1933, **140**, *A*, 440). Nevertheless, the method possesses practical advantages and has often given useful results (for references see Dippy, *Ann. Reports*, 1941, **38**, 132). Some of the theoretical difficulties can be avoided by considering the ratio of the first to the second dissociation constant of a dibasic acid (K_1/K_2). The present paper describes measurements of the thermodynamic dissociation constants of benzoic, adipic, succinic, and *cis*-tetrahydronaphthalene-2 : 3-dicarboxylic acids, and of methyl hydrogen succinate, in aqueous ethyl alcohol and in aqueous dioxan. The dissociation constants of benzoic acid in the same solvents have also been measured approximately by the use of cells not involving liquid junctions; this was done since dissociation constants have frequently been expressed with reference to that of benzoic acid.

EXPERIMENTAL.

Materials.—Ordinary absolute ethyl alcohol was refluxed over lime and distilled. The small water content of the distillate was estimated from the density, and the calculated weights of alcohol and carbon dioxide-free distilled water were mixed to give the required solvents. Commercially purified dioxan was refluxed over sodium and fractionally crystallised twice (Hess and Frahm, *Ber.*, 1938, **71**, 2627), the setting point then being 10·8°. Aqueous dioxan was made up by weighing. The compositions, densities, and dielectric constants (the last from the data of Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4130, and of Åkerlöf and Short, *ibid.*, 1936, **58**, 1241) at 20·0° of the mixed solvents used are shown in Table I.

TABLE I.

Solvent.	Organic liquid, % by wt.	*d*.	*D*.	*A*.
H_2O	—	0·998	80·4	0·50
H_2O–C_2H_5·OH	25	0·965	65·7	0·68
H_2O–C_2H_5·OH	50	0·919	50·4	1·01
H_2O–$C_4H_8O_2$	30	1·025	53·3	0·93

Pure commercial benzoic, adipic, and succinic acids were thrice recrystallised from water; *cis*-tetrahydronaphthalene-2 : 3-dicarboxylic acid (Haworth and Slinger, J., 1940, 1321) was recrystallised once. Methyl hydrogen succinate, prepared by the method of Bone, Sudborough, and Sprankling (J., 1904, **85**, 539) and twice recrystallised from carbon tetrachloride, had m. p. 57°.

Method of Measurement.—Solutions of the acids (0·0005—0·002M) were potentiometrically titrated at 20·0° with approximately 0·05N-sodium hydroxide (carbonate-free), the glass electrode being used. The liquid junction between the working solution and the bridge, containing saturated aqueous potassium chloride and leading to the standard half-cell, was made in the doubly bent capillary tube at the end of the bridge. Further details, including the method of standardising the pH scale and of calculating thermodynamic dissociation constants, have already been described (J., 1940, 855). (A similar method of calculation has since been given by Gale and Lynch, *J. Amer. Chem. Soc.*, 1942, **64**, 1153.) The alkali solutions were made up in the same solvent as the acid, except in some of the experiments in 25% aqueous alcohol, for which aqueous sodium hydroxide was used; the error thus introduced by the slight change in the water content of the medium during titration was negligible. The activity coefficients needed were worked out from the Debye–Hückel limiting law, $-\log f = z^2A\sqrt{I}$, z being the valency and I the ionic strength, and the values of A being those shown in Table I.

Dissociation constants, initially calculated in terms of molarities, have been converted to the molality basis by increasing pK ($= -\log_{10}K$) by $\log_{10}d$, where d is the density of the solvent. Results, including those for water (J., 1940, 895; 1941, 490) and each the mean of several independent determinations, are given in Table II. The accuracy is estimated at ± 0·05 unit in pK, and rather better in ΔpK.

Error of Glass Electrode in Mixed Aqueous Solvents.—Although the glass electrode has been used successfully in mixed aqueous solvents (*e.g.*, by Bennett, Brookes, and Glasstone, J., 1935, 1821), it may become subject to errors when the proportion of water becomes low (cf. Goodhue and Hixon, *J. Amer. Chem. Soc.*, 1935, **57**, 1688; Dole, "The Glass Electrode," p. 140). For this reason the present work was not extended to solvents containing less than 50% by weight of water. In 50% aqueous alcohol the activity of the water, $\{H_2O\}$, is 0·83; and the error of the glass electrode, if Dole's formula, $\Delta E = (RT/F)\ln\{H_2O\}$, is accepted, is − 0·0046 v., or + 0·08 pH unit. This is larger than the experimental error in the present work, but was neglected because its precise magnitude is uncertain and it seems likely to give rise

TABLE II.

Thermodynamic dissociation constants at 20·0°.

Solvent:	Water.			25% C_2H_5·OH.			50% C_2H_5·OH.			30% $C_4H_8O_2$.		
Acid.	pK_1.	pK_2.	ΔpK.	pK_1.	pK_2.	ΔpK.	pK_1.	pK_2.	ΔpK.	pK_1.	pK_2.	ΔpK.
Adipic	4·43	5·42	0·99	4·93	6·00	1·07	5·83	6·98	1·15	5·45	6·55	1·10
Succinic	4·22	5·67	1·45	4·65	6·19	1·54	5·48	7·24	1·76	5·19	6·84	1·65
Methyl hydrogen succinate	4·56	—	—	5·03	—	—	5·89	—	—	5·43	—	—
cis-Tetrahydronaphthalene-2 : 3-dicarboxylic	3·98	6·47	2·49	4·48	7·59	3·11	5·27	8·85	3·58	4·99	8·33	3·34
Benzoic	4·24	—	—	4·83	—	—	5·87	—	—	5·35	—	—

to a consistent error. It was observed that, as the percentage of water in the solvent diminished, the electrode needed longer to respond to changes of pH during titration.

Measurements using Cells without Liquid Junctions.—Approximate measurements were made of the dissociation constants of benzoic acid in the same solvents by use of cells not involving liquid junctions (cf. Harned, *Chem. Reviews*, 1939, **25**, 31). The cells were of the type Ag|AgCl|solution|quinhydrone|Pt, the solution being 0·1-molal hydrogen chloride or a benzoic acid–benzoate buffer containing sodium chloride and of total ionic strength about 0·006. The E.M.F., along with the activities of hydrogen chloride in the respective solvents obtained by interpolation from the data of Butler and Robertson (*Proc. Roy. Soc.*, 1929, **125**, *A*, 694) for aqueous alcohol and of Harned and Morrison (*J. Amer. Chem. Soc.*, 1936, **58**, 1908) for aqueous dioxan, enabled the thermodynamic dissociation constants of the benzoic acid to be calculated by an unequivocal method. The usual procedure of extrapolation to zero ionic strength was omitted, since the above interpolation was not very certain, and the E.M.F. measurements had in consequence been made only approximately. Results are given in Table III, the estimated accuracy being ± 0·1 unit. These values differ but little

TABLE III.

Thermodynamic dissociation constants of benzoic acid at 20·0°.

(Cells without liquid junctions.)

Solvent.	H_2O.	25% C_2H_5·OH.	50% C_2H_5·OH.	30% $C_4H_8O_2$.
pK	$4·2_2$	4·7	$5·6_5$	5·2

from those found by the other method (Table II), and the differences would be even smaller had allowance been made for the error of the glass electrode in the mixed solvents. In this particular instance, at least, the uncertainties involved in the use of cells with liquid junctions have not led to any very considerable errors.

The nature of these uncertainties has been indicated by Guggenheim (*e.g., J. Physical Chem.*, 1929, **33**, 842; 1930, **34**, 1758; *Phil. Mag.*, 1936, **7**, 983). The thermodynamic dissociation constants of an acid (HA) in two solvents (s and t) are defined by the equations.

$$K_s = \{H^+\}_s\{A'\}_s/\{HA\}_s \quad . \quad . \quad . \quad . \quad (1) \qquad \text{and} \qquad K_t = \{H^+\}_t\{A'\}_t/\{HA\}_t \quad . \quad . \quad . \quad (2)$$

{} indicating activities, and the subscripts indicating that these are referred, as usual, to infinite dilution in the respective solvents. The experimental arrangement used in attempting to compare K_s and K_t by use of cells with liquid junctions consists in principle of a cell of the type:

$$+H_2|\text{Buffer solution in s}|\underbrace{\text{Satd. KCl}}_{E_D}|\text{Buffer solution in t}|H_2-$$

$$\{H^+\}_s \qquad\qquad \{H^+\}_t$$
$$\{A'\}_s = [A']_s f_s^1 \qquad\qquad \{A'\}_t = [A']_t f_t^1$$
$$\{HA\}_s = [HA]_s f_s^0 \qquad\qquad \{HA\}_t = [HA]_t f_t^0$$

The E.M.F. of this cell can be expressed by the equation

$$E = (RT/F)\ln\{H^+\}_s/\{H^+\}_{t/s} + E_D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The double subscript t/s is now added to the activity appearing in the denominator since $\{H^+\}_t$ and $\{H^+\}_s$ are expressed on different scales, and the quantity obtained by the use of equation (3) is related to the former by the relationship $\{H^+\}_{t/s}/\{H^+\}_t = l$, in which l is the distribution ratio for hydrogen ions between s and t—a quantity which, like E_D, is not accessible to measurement. Substituting in (3), we have:

$$E - \left(E_D - \frac{RT}{F}\ln l\right) = \frac{RT}{F}\ln\frac{K_s}{K_t} + \frac{RT}{F}\ln\frac{[HA]_s[A']_t}{[HA]_t[A']_s} + \frac{RT}{F}\ln\frac{f_s^0 f_t^1}{f_t^0 f_s^1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In general, we cannot find the ratio K_s/K_t because we do not know the terms in parentheses on the left-hand side of (4). These terms being neglected, and the activity coefficients being estimated in the conventional manner (by use of the Debye–Hückel limiting law for the ions), let the ratio actually found be K_s/K_t' [K_t' will in general differ from K_t: Michaelis and Mizutani call it the "reduced dissociation constant" (cf. the "acidity function" of Brönsted)]. The dissociation constants given in Table II (and the results of many previous workers in this field) really correspond to K_t'. The fact that for benzoic acid K_t' (Table II) and K_t (Table III) do not differ substantially suggests that the terms neglected are together small. Indeed, it seems possible that they might individually act in opposite directions: s being water and t (for example) aqueous alcohol, it seems reasonable to suppose that l should be greater than unity; whilst E_D would be expected to be positive since the dielectric constant of s is the greater. In any case it seems that $E_D - (RT/F)\ln l$ could be determined for any pair of solvents by comparing the dissociation constants of a given acid as found by the two methods; l would be constant, and, if E_D were reproducible and independent of the nature of the acid (as is likely), true thermodynamic dissociation constants of other acids in the two solvents could then be compared by the use of cells with liquid junctions.

DISCUSSION.

Bjerrum (*Z. physikal. Chem.*, 1923, **106**, 219) derived a simple relationship (5) between the first and the second dissociation constant of a symmetrically dibasic acid; e is the electronic charge, k the Boltzmann

constant, D the dielectric constant of the solvent, and R the distance between the negative poles in the double anion. The formula implies that the anion can be replaced by a model consisting of two point charges a

$$\Delta pK - \log 4 = e^2/(2{\cdot}3kTDR) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

distance R apart and having extension in one dimension only. This is an obvious over-simplification, but gives reasonable values of R provided it be not too small. When R is small, its value calculated from (5) is improbably low (*e.g.*, 3·7 A. for succinic acid).

It is convenient, following Eucken (*Z. angew. Chem.*, 1932, **45**, 203), to replace (5) by (6), in which D_E is the effective dielectric constant of the region between the negative poles. Attempts can then be made to

$$\Delta pK - \log 4 = e^2/(2{\cdot}3kTD_ER) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

calculate D_E. Ingold (J., 1931, 2179; see also Jones and Soper, J., 1936, 133) has considered the effect of the field near the ion in modifying the properties of the solvent (water) locally; the ion was still regarded as of negligible bulk. Kirkwood and Westheimer (*J. Chem. Physics*, 1938, **6**, 506, 513; note errata, *ibid.*, 1939, **7**, 437, and others) have taken account of the fact that the region around and between the poles is occupied, not by solvent but by the body of the acid molecule, which for most organic acids may be regarded as having a low dielectric constant. They made calculations on the bases of two models which were convenient for mathematical treatment. The first represented the molecule by a sphere of dielectric constant 2 immersed in water ($D = 78$), with two point charges embedded in it; by the methods of spherical harmonics D_E was calculated as a function of the positions of the charges. The second (more suited for elongated molecules) represented the molecule by an ellipsoid of revolution with the charges at the foci; D_E was calculated as a function of the eccentricity of the ellipsoid. These calculations led to the surprising result that D_E can exceed the value of D for the solvent, and that it does so for positions of the charges corresponding to probable physical conditions [*viz.*, with the spherical model, when the charges are at, or near, the surface of the sphere; with the ellipsoidal, when the eccentricity exceeds a value of about 0·77 (*i.e.*, when λ_0 is less than 1·3) which corresponds to a molecule of quite moderate elongation]. This result is opposed to empirical requirements in most cases where the simple Bjerrum relationship breaks down.

Restricting ourselves to the ellipsoidal model, which more closely represents the structures of the acids dealt with here, the ellipsoid is described by the interfocal distance, R, and by the equation $\lambda = \lambda_0$, where λ is the confocal co-ordinate defined by $\lambda = (r_1 + r_2)/R$, r_1 and r_2 being the distances of any point from the foci. Closer agreement with experiment is reached if Westheimer and Kirkwood's expression for D_E is replaced by the simplified, empirical equation (7). D is the dielectric constant of the solvent in bulk, D_1 that of the molecule of the acid and assumed to be 2 (as for a paraffin), and P_n and Q_n are the Legendre polynomials of the first and the second kind.

$$\frac{1}{D_E} = \frac{1}{D_1} - \left(\frac{1}{D_1} - \frac{1}{D}\right)\left\{\sum_{n=0}^{\infty} 2(2n+1)\frac{Q_n(\lambda_0)}{P_n(\lambda_0)}(-1)^n\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Equation (7) can be deduced from the model by postulating an appropriate contact potential at the surface between the ellipsoid and the surrounding medium—a procedure of questionable validity—but it has the advantage of giving values of D_E which rise to, but do not exceed, D as λ_0 diminishes to unity. Values of the quantity in brackets (Σ) and of D_E for water and aqueous alcohol at 20° are shown in Table IV.

TABLE IV.

λ_0	1·0	1·1	1·2	1·3	1·4	1·6
Σ	(1·000)	0·99995	0·9988	0·9929	0·981	0·941
D_E ($D = 80{\cdot}4$ (water))	80·4	80·2	76·6	62·9	46·0	24·4
D_E ($D = 50{\cdot}4$ (50% alcohol))	50·4	50·3	48·9	43·0	34·5	20·8

Combination of (7) with the Eucken equation (6) suggests that ΔpK should be a linear function of $1/D$, and that the limiting value of ΔpK obtained by extrapolation to $1/D = 0$ should be larger than log 4, the value to be expected from the Bjerrum formula (5). The results quoted in Table II are in general agreement with these expectations. ΔpK values in aqueous dioxan, however, fall rather below the line for those in aqueous alcohol. The composition of a mixed solvent in the neighbourhood of a dissolved ion will generally differ from that of the solvent in bulk owing to the operation of the salting-out effect (cf. Elliott and Kilpatrick, *J. Physical Chem.*, 1941, **45**, 485), and the extent of this effect may differ as between alcohol and dioxan. Aqueous dioxan acts here as if it had a higher effective dielectric constant than an aqueous alcohol of the same bulk dielectric constant. This situation is also reflected in the pK values themselves.

The volume (V) of an ellipsoid of revolution is given by $(\lambda_0^3 - \lambda_0) = 6V/\pi R^3$. For succinic and adipic acids R has been calculated by assuming the polymethylene chain to be an extended zigzag, with the C–C distance 1·54 A. and the C–C–C angle 111½° (cf. Gane and Ingold, J., 1931, 2165; also *Ann. Reports*, 1940, **37**, 176; J., 1941, 940). The negative charges on the carboxylate groups were taken to be 1·0 A. beyond the terminal carbon atoms. V has been estimated from Traube's rule of the additivity of molecular volumes in solution (*Annalen*, 1895, **290**, 44). Details are shown in Table V, whence it appears that the calculated values of ΔpK are in agreement with experiment.

TABLE V.

		Succinic acid.	Adipic acid.
Volume of ion	(c.c./mole)	76·2	108·4
	(A.³/molecule = v)	127	180
Distance between charges (R)		5·9	8·3
λ_0		1·38	1·20
Solvent: water	D_E	49·5	76·5
	ΔpK (calc.)	1·46	0·99
	ΔpK (obs.)	1·45	0·99
Solvent: 50% alcohol	D_E	36·5	49·0
	ΔpK (calc.)	1·77	1·20
	ΔpK (obs.)	1·76	1·15

Simple considerations lead to the expectation that the dissociation constant of methyl hydrogen succinate (K) should be half as great as the primary dissociation constant of succinic acid (K_1); *i.e.*, $pK - pK_1 = 0{\cdot}30$. This expectation is fulfilled in water, and approximately in aqueous dioxan; but in aqueous alcohol ($pK - pK_1$) exceeds 0·30 by more than the experimental error.

THE UNIVERSITY, SHEFFIELD, 10. [*Received, March 20th*, 1943.]

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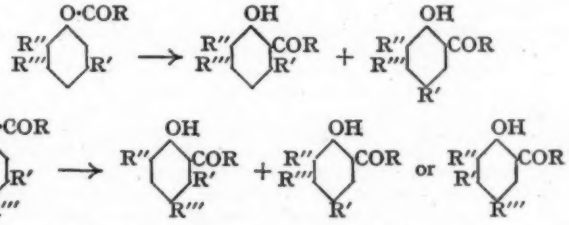
71. *The Fries Rearrangement and Subsequent Isomerisation.*

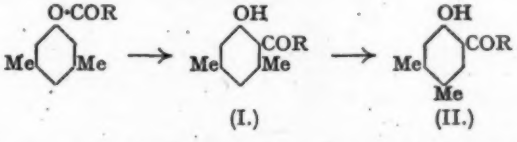
By G. BADDELEY.

The migration of one alkyl group sometimes observed in the Fries rearrangement is not conditioned by the presence of another alkyl group in the *p*-position to it. The isomerisation has been studied kinetically.

AUWERS (*Annalen*, 1928, **460**, 254) has tabulated a number of instances in which the normal product of the Fries rearrangement was accompanied by an isomeride, derived by displacement of an alkyl group from its original position:



Although in all the instances recorded by Auwers, a second alkyl group was in the *p*-position to that displaced, this is not essential. It has been shown that the acetate, propionate, and benzoate of *m*-5-xylenol are convertible quantitatively into either the corresponding 6-hydroxy-2 : 4-dimethylphenyl alkyl or aryl ketone (I) or its 3 : 4-dimethyl isomeride (II) according as only 1 mol. or 2 or more mols. of aluminium chloride are used. Auwers obtained mixtures of isomerides because he used 1—2 mols. of the chloride.



(I.) (II.)

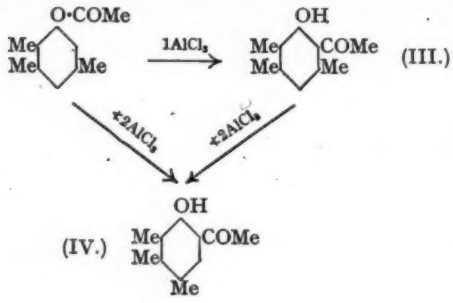
As would be expected from these results, hydroxy-ketones of type (I) undergo isomerisation when treated with 2 or more mols. of aluminium chloride. The reaction is bimolecular and the table summarises the results obtained with 3 and 3·5 mols. of reagent:

Phenol.	Acid.	Temp.	k.	E (Cals.).	Phenol.	Acid.	Temp.	k.	E (Cals.).
m-5-Xylenol	Propionic	140°	0·179	—	*m*-5-Xylenol	Benzoic	160°	0·107	—
		150	0·359	24·2			170	0·209	25·6
,,	Acetic	140	0·177	—	3 : 5-Diethylphenol	Acetic	110	0·405	—
		150	0·357	24·4			130	1·47	19·9

An experiment in which (I, R = Me) was isomerised in the presence of an added amount of (II, R = Me) showed that these hydroxy-ketones make respectively one and two molecules of reagent ineffective for producing the isomerisation.

The greater mobility of the ethyl than of the methyl group demonstrated by these results accords with various observations of Auwers, according to which, for example, both 2 : 5-dimethyl-4-ethyl- and 2 : 4-dimethyl-5-ethyl-phenyl acetates were isomerised to 6-hydroxy-3 : 5-dimethyl-4-ethylacetophenone.

More highly alkylated compounds are also subject to the above generalisations. For instance, *iso*-ψ-cumenyl acetate yields either 2 : 4 : 5- or 3 : 4 : 5-trimethyl-6-hydroxyacetophenone (III and IV respectively). In such cases the extra alkyl group so facilitates the isomerisation of the ketone first formed that this sets in before a homogeneous reaction mixture can be prepared, and, so far, has prevented a kinetic investigation of the change.



Discussion of the theoretical significance of the results is postponed pending an account of similar studies of the isomerisation by aluminium chloride on the one hand of alkyl ketones and on the other of alkyl phenols. Meanwhile it may be pointed out that, since the acetyl group can be removed from 2-hydroxyacetophenones by hydrolysis, a convenient method is available for preparing, for example, *o*-4-xylenol from *m*-5-xylenol.

Experimental.

The 6-hydroxy-2 : 4-dimethyl derivatives of the following ketones were obtained quantitatively from the corresponding esters and aluminium chloride (1 mol.) at 120—150° : Acetophenone, stout, pale yellow needles, m. p. 60°, from light petroleum (b. p. 40—60°) (Auwers and Borsche, *Ber.*, 1915, **48**, 1707, give m. p. 58°); propiophenone, colourless needles, m. p. 78°, from light petroleum (b. p. 60—80°) (Found : C, 74·1; H, 7·8. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%); benzophenone, colourless needles, m. p. 143°, from ethyl alcohol (Wittig, Oppermann, and Faber, *J. pr. Chem.*, 1941, **158**, 61, give m. p. 139—140°).

The 6-hydroxy-3 : 4-dimethyl derivatives of the following ketones were similarly obtained : Acetophenone, colourless hexagonal plates, m. p. 74°, from light petroleum (b. p. 60—80°) (Auwers, Bundesmann, and Weiners, *Annalen*, 1926, **447**, 176, give m. p. 71°); propiophenone, colourless plates, m. p. 60°, from light petroleum (b. p. 60—80°) (Found : C, 74·2; H, 8·0. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%); benzophenone, pale yellow plates, m. p. 111°, from ethyl alcohol (Found : C, 79·8; H, 6·1. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%).

Each of the above 6-hydroxy-2 : 4-dimethyl derivatives isomerised quantitatively to the corresponding 6-hydroxy-3 : 4-dimethyl derivative when heated for several hours with aluminium chloride (3 mols.) at 140—180°. Similarly, 6-hydroxy-2 : 4-diethylacetophenone [the *dibromo*-derivative crystallised from light petroleum (b. p. 60—80°) in large colourless prisms, m. p. 81° (Found : Br, 45·8. $C_{12}H_{14}O_2Br_2$ requires Br, 45·7%)] isomerised to the 6-hydroxy-3 : 4-diethyl derivative [the *monobromo*-derivative crystallised from light petroleum (b. p. 60—80°) in small, pale yellow prisms, m. p. 59° (Found : Br, 29·6. $C_{12}H_{15}O_2Br$ requires Br, 29·5%)].

Quantitative Investigations.—Isomerisation of 6-hydroxy-2 : 4- to 6-hydroxy-3 : 4-dimethyl-acetophenone. Preliminary experiments determined the procedure for the simultaneous dibromination of the former and monobromination of the latter ketone.

A mixture of *m*-5-xylenyl acetate (10·2 g.), aluminium chloride (24·6 g.), and sodium chloride (2·4 g.) was heated at 120° in a rotating flask; the evolution of hydrogen chloride was complete in less than 30 minutes. The homogeneous liquid was divided between two flasks in thermostats at 140° and 150°. From time to time, portions of the mixture were transferred to a weighed flask and dissolved in 75% acetic acid (33·33 c.c./g. of mixture). The clear solution (5 c.c.) was pipetted into a 100 c.c. flask, 75% acetic acid (10 c.c.), carbon tetrachloride (3 c.c.), N/10-bromate–bromide (2·0—2·5 c.c. excess), and dilute hydrochloric acid (5 c.c.) added, and the mixture shaken for 3 minutes. Potassium iodide was added, followed, after 1 minute, by N/10-thiosulphate until the end-point was nearly reached; the flask was then almost filled with water, starch solution added, and the titration completed.

Temperature = 140°.

Time, hours.	Mixture, g.	Dilution, 75% AcOH, c.c.	0·1N-Bromate, c.c.	*k*.	Time, hours.	Mixture, g.	Dilution, 75% AcOH, c.c.	0·1N-Bromate, c.c.	*k*.
0	1·167	38·90	10·50	—	2·5	0·793	26·43	7·73	0·177
0·5	0·972	32·40	9·70	0·173	3·5	0·523	17·43	7·15	0·179
1·0	0·546	18·20	9·03	0·177	5·5	0·643	21·43	6·50	0·173
1·5	0·694	23·13	8·50	0·179	10·5	0·588	19·60	5·68	0·179
2·0	0·636	21·20	8·07	0·179	∞	—	—	5·25	—

Mean 0·177

$$k = \frac{1}{t - t_0} \ln \frac{T_t(T_0 - T_\infty)}{T_0(T_t - T_\infty)}.$$

The velocity constants tabulated on p. 273 were similarly obtained.

Isomerisation of 6-hydroxy-2 : 4- in presence of 6-hydroxy-3 : 4-dimethyl-acetophenone. A mixture of *m*-5- and *o*-4-xylenyl acetates (5·1 g. of each), aluminium chloride (25·2 g.), and sodium chloride (2·4 g.) gave $k_{150°} = 0{\cdot}354$, the hydroxy-ketones being assumed to use up 1 and 2 mols. of reagent respectively.

iso-*ψ-Cumenyl Acetate and Aluminium Chloride.*—The Fries rearrangement with 1 mol. of reagent gave a product, m. p. 46°, which isomerised to 6-hydroxy-3 : 4 : 5-trimethylacetophenone, m. p. 42° (Auwers, Bundesmann, and Weiners, *loc. cit.*, give m. p. 42°), when heated with 2 mols. of reagent. A mixture of the two products showed a marked depression of m. p.

I am indebted to Professor J. Kenner, F.R.S., for his interest in the work.

Municipal College of Technology, Manchester.

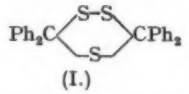
[*Received, June 8th*, 1942.]

72. *Photo-reactions. Part V. Photo-oxidation of Non-ionisable Thioketones in Sunlight.*

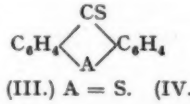
By A. Schönberg and Ahmed Mostafa.

Thiobenzophenone, a number of its derivatives, and 4-thiopyrones have been investigated with regard to their behaviour in benzene solution towards oxygen in the presence and in the absence of sunlight. Thiobenzophenone is oxidised even in the dark, yielding benzophenone.

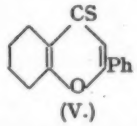
It is well known that solid thiobenzophenone is extremely sensitive to oxygen under normal laboratory conditions (Gattermann and Schulze, *Ber.*, 1896, **29**, 2944), being converted into benzophenone and the trisulphide (I) (Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1380, 2175; Staudinger and Freudenberger, *ibid.*, p. 1836). We have now found that thiobenzophenone is converted into benzophenone even in the absence of light. On the other hand, 4 : 4′-dimethoxythiobenzophenone, 4 : 4′-bisdimethylaminothiobenzophenone, xanthione (II), and thioxanthione (III) in benzene solution (thiophen-free) are stable or almost completely stable to oxygen in the dark, but are readily converted into the corresponding ketones in sunlight,* sulphur and sulphur dioxide being formed; *N*-phenylthioacridone (IV), 4-thioflavone (V), and 2 : 6-diphenyldithiopyrone (VI) are stable or almost completely stable both in the dark and in sunlight.



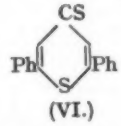
(I.)



(II.) A = O. (III.) A = S. (IV.) A = NPh.



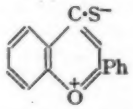
(V.)

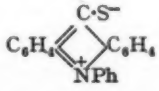


(VI.)

In order to explain the fact that the last three substances are not affected by oxygen in sunlight, it may be pointed out that they are not thioketones proper, but have the structure of zwitterions (compare VII and VIII in the case of 4-thioflavone and *N*-phenylthioacridone respectively) or that the zwitterion structure makes a great contribution to their resonance structure.

(VII.)





(VIII.)

The zwitterion structure of some of these thioketones and of related thioketones has been discussed by Arndt, Scholz, and Nachtwey (*Ber.*, 1924, **57**, 1903), who connect it with their colour, and by Weizmann (*Trans. Faraday Soc.*, 1940, **36**, 978), who draws her conclusions from the high dipole moment of some heterocyclic thioketones, *e.g.*, *N*-methylthioacridone.

Experimental.

Action of Oxygen on Thiobenzophenone in the Dark.—Oxygen was passed for 5 hours through sodium hydroxide solution, concentrated sulphuric acid, a safety tube, a dry benzene solution of thiobenzophenone (0·5 g.), a second safety tube, a tube containing wet potassium chromate paper, a tube containing mercuric sulphate solution, and finally a calcium chloride tube, the tubes being completely covered with dark paper. (All the tubes used in this and the following experiments were of Pyrex glass.) The intense blue colour of the thiobenzophenone solution faded gradually, and a colourless crystalline substance separated, which was proved to be sulphur by means of benzyliminodi-(4-methoxyphenyl)-methane (micro-method for the detection of elementary sulphur; Schönberg and Urban, *Ber.*, 1934, **67**, 1999). After removal of the solid the benzene filtrate was evaporated in a vacuum, and the residual oil inoculated with a crystal of benzophenone. The product, after recrystallisation from benzene, did not depress the m. p. of benzophenone. During the experiment the potassium chromate paper became green and a crystalline precipitate appeared in the mercuric sulphate solution, indicating the evolution of sulphur dioxide (compare Tables of Reagents for Inorganic Analysis, Leipzig, 1938, Akademische Verlagsgesellschaft M.B.H.).

Action of Oxygen on Thioketones.—(a) *In the dark.* 4 : 4′-Dimethoxythiobenzophenone, 4 : 4′-bisdimethylaminothiobenzophenone, xanthione (II), thioxanthione (III), *N*-phenylthioacridone (IV), 4-thioflavone (V), and 2 : 6-diphenyldithiopyrone (VI), dissolved in dry benzene, were treated for a week in darkness with oxygen under the conditions described above. They all remained unchanged or almost completely unchanged and no sulphur dioxide could be detected.

(b) *In sunlight.* Parallel experiments were carried out with the same thioketones.

The intense blue colour of the 4 : 4′-dimethoxythiobenzophenone solution changed to reddish and then orange-yellow. After evaporation of the benzene in a vacuum the yellow residue was proved to contain elementary sulphur and 4 : 4′-dimethoxybenzophenone, which was obtained pure after crystallisation from absolute ethyl alcohol. The presence of sulphur dioxide was shown as before.

The colours of the solutions of 4 : 4′-bisdimethylaminothiobenzophenone, xanthione, and thioxanthione faded. The products, isolated as before and crystallised from absolute ethyl alcohol, did not depress the m. p.'s of authentic 4 : 4′-bisdimethylaminobenzophenone, xanthone, and thioxanthone respectively.

4-Thioflavone, *N*-phenylthioacridone, and 2 : 6-diphenyldithiopyrone, after a week's treatment, were recovered unchanged or nearly unchanged.

Comparative Rates of Oxidation of Thioketones and 4 : 4′-Dimethoxythiobenzophenone.—(1) 4 : 4′-Dimethoxythiobenzophenone and 4 : 4′-bisdimethylaminothiobenzophenone in molecular proportion were each dissolved in 10 c.c. of dry benzene (thiophen-free). Oxygen was passed through sodium hydroxide solution, concentrated sulphuric acid,

* The different m. p.'s reported for various thioketones may be due to partial conversion into the corresponding ketones by the action of air in the presence of light during crystallisation. These thioketones should be crystallised in the dark.

a safety tube, the benzene solution of 4 : 4′-bisdimethylaminobenzophenone, the benzene solution of 4 : 4′-dimethoxythiobenzophenone, a third safety tube, and finally a calcium chloride tube. After 3 hours the solution of 4 : 4′-dimethoxythiobenzophenone had lost its blue colour and become slightly orange and when it was shaken with water the aqueous layer became colourless and the benzene layer faintly yellow (formation of a small amount of a red by-product or perhaps due to a small amount of impurity in the original material). When the 4 : 4′-dimethoxythiobenzophenone had been almost completely oxidised, a large amount of 4 : 4′-bisdimethylaminothiobenzophenone could still be recovered from its solution.

(2) The experiment was repeated, xanthione being used instead of 4 : 4′-bisdimethylaminobenzophenone. When the 4 : 4′-dimethoxythiobenzophenone had been almost completely converted into the corresponding ketone, a large amount of xanthione could be recovered.

(3) 4 : 4′-Dimethoxythiobenzophenone was oxidised before thioxanthione under the same conditions.

FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, August 17th*, 1942.]

73. *Photo-reactions. Part VI. Formation of Benzpinacol by the Action of Acetone on Benzhydrol in Sunlight.*

By ALEXANDER SCHÖNBERG and AHMED MOSTAFA.

IT is known that benzophenone is reduced to benzpinacol by *iso*propyl alcohol in sunlight (Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 394; *Org. Synth.*, Vol. 14, p. 8). We find that benzpinacol is also formed by the action of acetone (or methyl ethyl ketone) on benzhydrol in sunlight; the reaction proceeds rapidly and the product can be easily isolated :

$$2CHPh_2{\cdot}OH + COMe_2 \xrightarrow{\text{sunlight}} OH{\cdot}CPh_2{\cdot}CPh_2{\cdot}OH + CHMe_2{\cdot}OH$$

The preparation succeeds also in a sealed tube which does not contain oxygen and is therefore not due to partial oxidation of benzhydrol to benzophenone, which, as was found by Cohen (*Rec. Trav. chim.*, 1919, **38**, 113), reacts with benzhydrol to give benzpinacol.

EXPERIMENTAL.

Photo-reaction between Benzhydrol and Acetone.—A solution of benzhydrol (4 g.) in 20 c.c. of dry acetone (AnalaR) was exposed in a sealed Pyrex glass tube, in the absence of air, to direct sunlight for 8 hours (during May). The yellow solution was distilled in a vacuum (distillate A), and the crystalline residue recrystallised from absolute ethyl alcohol; it had m. p. 187°, not depressed by authentic benzpinacol (Bachmann, *loc. cit.*). The yield was about 50% (Found : C, 85·1; H, 6·1. Calc. for $C_{26}H_{22}O_2$: C, 85·2; H, 6·0%). A Monax glass vessel closed with a cork may be used if the absence of oxygen is not required. The experiment was repeated in winter time; after exposure for 10 days to direct sunlight (cloudy weather in December), the yield was about 70%.

The product was further identified by its interaction with pyridinium chloride to form tetraphenylglycolpyridinium chloride (Schönberg and Michaelis, J., 1936, 1571).

The distillate (A) was refluxed for 2 hours with an excess of *p*-nitrobenzoyl chloride; on cooling, a solid separated. The whole was dissolved in ether, and the solution washed with cold dilute aqueous sodium hydroxide, dried over anhydrous sodium sulphate, and distilled in a vacuum. The oily residue solidified on cooling; after crystallisation from hot ethyl alcohol it had m. p. 111°, not depressed by authentic *iso*propyl *p*-nitrobenzoate (Buchner and Meisenheimer, *Ber.*, 1905, **38**, 627). Yield, 2·5 g. When acetone was exposed to sunlight in the absence of air and treated with *p*-nitrobenzoyl chloride as described above, *iso*propyl *p*-nitrobenzoate was not detected.

Photo-reaction between Benzhydrol and Methyl Ethyl Ketone.—Benzhydrol (1 g.) and methyl ethyl ketone (1 mol.) in 20 c.c. of dry benzene (thiophen-free) were exposed in a sealed Pyrex glass tube to direct sunlight for 1 month (October—November). The benzene was removed in a vacuum, and the solid which separated from the residue on cooling was washed with benzene and crystallised from light petroleum (b. p. 100—110°); it had m. p. 187°, not depressed by authentic benzpinacol.

Photo-reaction between Benzhydrol and Benzophenone.—In a similar experiment, benzhydrol (1 g.) and benzophenone (1 mol.) were exposed to direct sunlight for 2 days (December). The benzene was driven off in a vacuum, and the crystalline residue recrystallised from absolute ethyl alcohol; it had m. p. 187°, not depressed by authentic benzpinacol. Yield, 80% (Found : C, 84·8; H, 6·1%).

FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, March 3rd*, 1943.]

74. *The Kinetics of Aromatic Halogenation. Part I. Bromination.*

By P. W. ROBERTSON, P. B. D. DE LA MARE, and W. T. G. JOHNSTON.

The bromination of acetanilide, aceto-*p*-toluidide, mesitylene, anisole, and *p*-tolyl methyl ether in acetic acid at room temperature shows in the concentration region M/40 third-order kinetics. This reaction, which has a low heat of activation, changes over to a bimolecular reaction at lower concentrations, with a higher *E* value. Addition of water to the solvent favours a bimolecular change, and addition of chloroform and carbon tetrachloride causes the initiation of chain reactions, with reaction order greater than 3. There is a formal similarity in mechanism between aromatic bromination and the addition of bromine to olefinic compounds.

THE study of bromine substitution reactions is complicated by the formation of HBr_3 which reduces the active Br_2 concentration. If the value of *K* for the reaction $HBr + Br_2 \rightleftharpoons HBr_3$ were known, a modified expression for the rate might be obtained, as was done by Bradfield, Jones, and Orton (J., 1929, 2810) for aqueous acetic acid solutions. For pure acetic acid, however, *K* varies with the concentration (Jones, J., 1911, **99**, 392).

A further complication is that the reaction is acid-catalysed, as found from experiments with added sulphuric acid for phenol ethers and hydrocarbons. On the other hand, acids reduce the bromination rate of bases such as acetanilide. These facts unduly complicate the interpretation. Ultimately a procedure was adopted depending on the following considerations. In the initial stages of the reaction the influence of the liberated hydrogen bromide is small, and this effect becomes progressively less, the smaller the proportion of bromine absorbed. If the concentrations of the reactants are now doubled, the relative influence of hydrogen bromide becomes greater, but its actual effect on n, the reaction order for these two concentrations, is not considerable, and becomes progressively smaller as x, the percentage of bromine absorbed, approaches zero. Accordingly, the first 20% change of the reactions was followed, and the values of n calculated for each 5% change. Owing to the relatively rapid change in rate with altered initial concentrations of reactants, some compounds could be investigated only at a high and others only at a low concentration range. Aceto-*p*-toluidide has an intermediate rate and its order of reaction was measured over the range indicated below, in acetic acid at 24·0°.

x, % of Br_2 absorbed	5	10	15	20
n (M/10—M/20)	3·1	3·3	3·4	3·3
n (M/20—M/40)	3·1	3·1	3·1	3·1
n (M/40—M/80)	3·1	3·1	3·1	3·1

These results indicate third-order kinetics in this concentration range, with a slight upward drift in k_3 coefficients with the concentration. The following compounds were also investigated in acetic acid at 24·0°.

x, % of Br_2 absorbed	5	10	15	20
Acetanilide, n (M/40—M/80)	2·9	2·9	2·9	3·0
Mesitylene, n (M/40—M/80)	2·9	3·1	3·2	3·3
p-Tolyl methyl ether n (M/40—M/80)	3·1	3·1	3·0	2·9
p-Tolyl methyl ether, n (M/80—M/160)	3·0	3·1	3·1	3·2
Anisole, n (M/80—M/160)	—	3·0	2·9	2·8

The participation of the reactants, A and Br_2, in these termolecular reactions was determined by rate measurements with $2A + Br_2$ and $A + 2Br_2$, and it was found that the reactions were bimolecular with respect to Br_2 and unimolecular with respect to A. Added sulphuric acid accelerated the reaction for anisole and mesitylene, but retarded it for acetanilide. This difference in behaviour is further revealed in a comparison of the k_3 coefficients for M/40-mesitylene and M/40-acetanilide for the reactions with M/40-bromine in acetic acid at 24·0° :

x, % of Br_2 absorbed	5	10	15	20	30	40	50
Mesitylene, k_3	870	920	940	920	870	840	820
Acetanilide, k_3	890	920	940	880	710	470	340

In the mesitylene reaction the acid catalysis increases as the reaction proceeds owing to formation of HBr and HBr_3 and offsets the fall in rate due to removal of bromine as HBr_3, whereas with acetanilide negative acid catalysis operates and the two effects combine to cause a rapid decrease in the k_3 values.

The reaction between bromine and acetanilide has been examined also at low concentrations in acetic acid at 24·0°. The relative rates are shown as bimolecular coefficients :

	M/20.	M/40.	M/80.	M/160.	M/320.	M/640.	M/1280.
k_2 ($x = 20$)	9·5	4·9	2·5	1·4	0·85	0·57	0·46
n	2·9	3·0	2·9	2·7	2·6	2·3	
E (cals.)	—	3,300	—	—	—	11,000	—

The termolecular process dominant at M/40 changes over to a second-order reaction in the region M/1000, and correspondingly the heat of activation increases. As the temperature coefficient of the bimolecular reaction is greater, the termolecular reaction must be gradually replaced with rise in temperature. The n value for the range M/40—M/80, which is 3·0 at 24°, becomes 2·5 at 50°.

The influence of water on the brominations in acetic acid is to increase the rate and to cause a gradual change over to second-order kinetics. The effect of non-ionising solvents such as chloroform or carbon tetrachloride is initially to decrease the rate. With larger amounts of these solvents the nature of the reaction changes : the order becomes greater than 3, and the reactions become light-sensitive. These differences indicate the incursion of an atom chain-reaction, which in pure chloroform or carbon tetrachloride becomes rapid and non-reproducible. This is shown in the following table.

Relative initial rates (n *values in parentheses*) *in acetic acid mixtures at* 24·0°.

$CHCl_3$	0	50%	75%	90%	100%
Anisole (M/80)	1 (3·0)	0·30 (2·8)	0·12 (3·1)	0·08 (3·6)	Variable
CCl_4	0	60%	90%	100%	
Acetanilide (M/40)	1 (2·9)	0·20 (3·5)	2·9 (5·7)	Variable	

The alteration in the character of the reaction on dilution of the solvent with carbon tetrachloride is strikingly illustrated by a comparison of the rates of bromination of acetanilide in acetic acid and in 90% carbon tetrachloride + 10% acetic acid, the relative rates for M/160-reactants at 24·0° being shown as bimolecular coefficients :

x, % of Br_2 absorbed	10	20	30	40	50	60
k_2 (HOAc)	1·56	1·34	1·16	0·92	0·75	0·55
k_2 (90% CCl_4 + 10% HOAc)	0·26	0·42	0·69	0·90	1·21	1·60

A similar type of curve was found for anisole in the same mixed solvent, indicating that the effect is not peculiar to the acetamido-group. Initially-added hydrogen bromide gave a very marked acceleration in rate, so the autocatalysis is due to the hydrogen bromide produced in the reaction.

Two compounds with relatively slow rates of bromination have been found to give reaction orders greater than 3 in acetic acid at 24·0° :

x, % of Br_2 absorbed	5	10	15	20
m-Xylene, n (M/5—M/10)	3·9	3·9	4·0	3·9
Naphthalene, n (M/5—M/10)	—	4·0	4·0	4·1
Naphthalene, n (M/10—M/20)	—	3·7	3·7	3·7
Naphthalene, n (M/20—M/40)	—	3·4	3·4	3·4

The fact that n does not increase as the reaction proceeds would seem to indicate that HBr_2 formation is not responsible for the order higher than 3. It is possible that atom chains may be formed even in acetic acid, becoming evident when the normal reaction is very slow. Dilution with carbon tetrachloride increases the contribution of the higher-order reaction, changing n for naphthalene from 4·0 to 4·5 in 50% carbon tetrachloride + 50% acetic acid.

As the possibility of chain reactions appears here to be indicated in aromatic brominations in acetic acid, it might be argued that the effects observed in the bromination reactions in acetic acid, *viz.*, the increase in reaction order from $n = 2$ on increasing the concentration, could be explained as due to the same cause. It is believed that this is not so, and that the increase in n to 3 at the concentration region M/40 is due to a gradual dominance of a termolecular reaction. The constancy of the n values for aceto-*p*-toluidide at $x = 5\%$ (see p. 277) is a fairly definite indication that over the range M/10—M/80 there is no appreciable chain reaction. When a chain reaction is indicated, *e.g.*, by the light-sensitivity of the reaction, increase in concentration causes n to become greater; for instance, acetanilide in 90% carbon tetrachloride + 10% acetic acid gives, for M/80—M/160, $n = 3{\cdot}4$, and for M/40—M/80, $n = 5{\cdot}7$.

Experimental.

The solvents, bromine, and general technique were as previously described (J., 1937, 335; 1939, 1510). The following compounds were used : acetanilide, m. p. 113°; aceto-*p*-toluidide, m. p. 148°; naphthalene, m. p. 80·0°; *m*-xylene, b. p. 138·0—138·5°/760 mm.; mesitylene, b. p. 165·0°/760 mm.; anisole, b. p. 151·5—152·0°/760 mm.; *p*-tolyl methyl ether, b. p. 174·0°/760 mm.

Rate measurements were carried out in duplicate or triplicate, the zero titration figure being obtained by mixing the bromine solution with acetic acid in a reaction bottle of similar dimensions, and titrating the same volume as that used for the reaction mixture. For the slow reactions this bottle was left in the thermostat for checking volatility losses (never >4%). From the curve relating t and x the values of t were read off at 5, 10, 15, and 20%, a small correction (never >1%) being made whenever the initial titre of the bromine varied from the normality under investigation. The following are the details of such a measurement.

M/20-*Aceto*-p-*toluidide* + M/20-Br_2 *in acetic acid at* 24·0°.
Reaction mixture, 10 ml.; 2 ml. samples titrated with 0·05N-$Na_2S_2O_3$.

Time (mins.)	0	2·60	7·40	30·00	0	4·12	14·10	24·7
Titre, ml.	4·06	3·89	3·67	3·16	4·06	3·80	3·46	3·23

The experimental times for aceto-*p*-toluidide, for which n values are shown in the first table, were :

x	5	10	15	20	x	5	10	15	20
t (mins.), M/10	0·75	1·62	2·82	5·01	t (mins.), M/40	14·0	33·5	62·0	101·5
t (mins.), M/20	3·2	7·9	14·7	23·9	t (mins.), M/80	60	149	270	440

For the compounds listed in the second table, the times (mins.) at $x = 10\%$ only are given : acetanilide, M/40, $t = 0{\cdot}82$; M/80, $t = 3{\cdot}02$; mesitylene, M/40, $t = 0{\cdot}82$; M/80, $t = 3{\cdot}55$; *p*-tolyl methyl ether, M/40, $t = 2{\cdot}10$; M/80, $t = 8{\cdot}9$; M/160, $t = 37{\cdot}3$; anisole, M/80, $t = 0{\cdot}54$; M/160, $t = 2{\cdot}09$.

The measurements to show the participation of the reactants were made with acetanilide (A) at 24·0° :

M/40-A + M/40-Br_2, t ($x = 20\%$ Br_2) 2·04; $k_2 = 4{\cdot}9$
M/80-A + M/40-Br_2, t ($x = 20\%$ A) 1·76; $k_2 = 5{\cdot}3$
M/40-A + M/80-Br_2, t ($x = 20\%$ Br_2) 3·82; $k_2 = 2{\cdot}5$
M/80-A + M/80-Br_2, t ($x = 20\%$ Br_2) 8·05; $k_2 = 2{\cdot}5$

The influence of acids and bases on bromination in acetic acid at 24·0° is shown, as the ratio of catalysed to uncatalysed reaction :

Acetanilide, reactants M/40, +0·15M-H_2SO_4 : 0·47
Mesitylene, reactants M/40, +0·10M-H_2SO_4 : 1·53
Anisole, reactants M/80, +0·012M-H_2SO_4 : 1·11

The times (mins.) for the values for acetanilide quoted in the fourth table are as follows (for $x = 20$) : At 24·0°, M/20, $t = 0{\cdot}53$; M/40, $t = 2{\cdot}04$; M/80, $t = 8{\cdot}05$; M/160, $t = 29{\cdot}8$; M/320, $t = 94{\cdot}0$; M/640, $t = 280$; M/1280, $t = 698$. At 16°, M/40, $t = 2{\cdot}27$. At 34·6°, M/40, $t = 1{\cdot}64$. At 34·8°, M/640, $t = 143$. At 49·0°, M/640, $t = 67{\cdot}4$.

The following measurements were made (for $x = 20$) in 20% water + 80% acetic acid : At 24·0° : M/640, $t = 1{\cdot}00$; M/1280, $t = 2{\cdot}03$ ($n = 2$). At 16·0°, M/640, $t = 1{\cdot}32$. At 35·6; M/640, $t = 0{\cdot}63$ ($E = 7{,}100$).

The following are the experimental details of the results quoted in the fifth table, the times being given for $x = 10\%$.

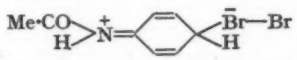
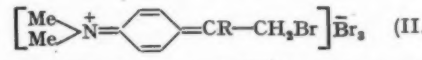
Anisole	50% $CHCl_3$, 50% HOAc :	M/80, $t = 2{\cdot}07$; M/160, $t = 7{\cdot}00$
	75% $CHCl_3$, 25% HOAc :	M/80, $t = 4{\cdot}35$; M/160, $t = 18{\cdot}7$
	90% $CHCl_3$, 10% HOAc :	M/80, $t = 4{\cdot}38$; M/160, $t = 27{\cdot}0$
Acetanilide	60% CCl_4, 40% HOAc :	M/40, $t = 4{\cdot}62$; M/80, $t = 26{\cdot}3$
	90% CCl_4, 10% HOAc :	M/40, $t \sim 0{\cdot}25$; M/80, $t = 11{\cdot}2$; M/160, $t = 65$

The experimental time values ($x = 10$) (sixth table) were: Naphthalene: M/5, $t = 4{\cdot}8$; M/10, $t = 38{\cdot}6$; M/20, $t = 260$; M/40, $t = 1405$. *m*-Xylene (HOAc + 1% H_2O): M/5, $t = 0{\cdot}82$; M/10, $t = 6{\cdot}22$.

The bromination of certain hydrocarbons has been investigated by Lauer and Oda (*Ber.*, 1936, **69**, 978) in 1% water + 99% acetic acid. Their results appear to be vitiated by grave errors. The following is characteristic, our data being compared with theirs (in parentheses): naphthalene + Br_2, 18°, reactants 0·161M; $t = 10$, $k_2 = 9{\cdot}0 \times 10^{-3}$ ($22{\cdot}7 \times 10^{-3}$); $t = 60$, $k_2 = 5{\cdot}5 \times 10^{-2}$ ($7{\cdot}0 \times 10^{-2}$); reactants 0·056M, $t = 10$, $k_2 \sim 1{\cdot}5 \times 10^{-2}$ ($33{\cdot}8 \times 10^{-2}$); $t = 60$, $k_2 = 1{\cdot}1 \times 10^{-2}$ ($7{\cdot}95 \times 10^{-2}$). The fact that the divergences are greater (*a*) with smaller t, (*b*) at lower initial concentrations, and (*c*) for more slowly reacting compounds, indicates the presence of unsaturated impurity in their solvent, and this is also apparent in Fig. 5 (*loc. cit.*, p. 982).

Discussion.

The bromination of acetanilide in acetic acid at 24° changes from a termolecular reaction at M/40 (E = 3,300) to a bimolecular reaction in the region M/1000 (E = 11,000). Under the same conditions bromine addition to allyl acetate, which proceeds at the same general rate, changes similarly in reaction order over the same concentration range, the values of E being respectively 4000 and 9000. Such a formal similarity cannot be regarded as accidental, and indeed can be explained as due to the operation of a similar rate-determining mechanism in the two reactions. A termolecular reaction may be considered kinetically as a simultaneous collision between three molecules, in this instance one of A and two of Br_2. If the time of contact between two of these molecular species becomes relatively considerable, the process may be regarded as proceeding *via* an intermediate compound, $(Br_2)_2$ or A,Br_2. An addition compound, Br–Br→Br–Br, in its various resonance forms, is theoretically possible. There is no evidence for the association of bromine in acetic acid, but for a mechanism showing third-order kinetics the concentration of $(Br_2)_2$ need be only very small. The second possibility, and this has equal theoretical justification, is that an intermediate, *e.g.*, (I) is formed This mechanism

(I.)   (II.)

is preferred, for substances similar to (I) have been obtained by Pfeffer and Wizinger (*Annalen*, 1928, **461**, 132) by the action of bromine on compounds of the type $(C_6H_4X)_2C{:}CH_2$, which undergo substitution in the ω-position. Thus, the isolation of (II) (R = $C_6H_4{\cdot}NMe_2$) represents the actual fixing of one of the stages in a process, which is similar for substitution and addition:

$$A + Br_2 \underset{2}{\overset{1}{\rightleftharpoons}} A,Br_2; \quad A,Br_2 + Br_2 \xrightarrow{3} A\overset{+}{B}r + \overline{B}r_3 \xrightarrow{\text{rapid}} \text{products}$$

By application of the method of stationary concentrations, the kinetic form of such a reaction is given by the expression:

$$-d[A]/dt = k_1k_3[A][Br_2]^2/(k_2 + k_3[Br_2])$$

If $k_3 \gg k_2$: $-d[A]/dt = k_1[A][Br_2]$ (second-order kinetics)
If $k_2 \gg k_3$: $-d[A]/dt = k_1k_3[A][Br_2]^2/k_2$ (third-order kinetics)

The reactions under consideration show within a given temperature and concentration range third-order kinetics, but the true bimolecular reaction may operate simultaneously. The latter is favoured by dilution, when the relative frequency of termolecular to bimolecular collisions decreases, and on raising the temperature, owing to the greater temperature coefficient of the bimolecular reaction. Addition of water to the solvent also favours second-order kinetics. Since E for the reactions in aqueous acetic acid is higher than that obtained for the termolecular change in pure acetic acid, it is concluded that the effect of water is to favour the bimolecular mechanism, rather than to cause the termolecular reaction to show second-order kinetics.

Victoria University College, Wellington, N.Z. [*Received, July 28th*, 1941.]

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75. *The Kinetics of Aromatic Halogenation. Part II. The Chlorination of Hydrocarbons.*

By P. B. D. de la Mare and P. W. Robertson.

The rates of chlorination of benzene and naphthalene, and the heats of activation, have been measured in acetic acid solution. The relative rates of chlorination of the series RPh, where R = Me, Et, Pr$^\beta$, Bu$^\gamma$, are in the order 100, 84, 51, 32, showing the operation of alkyl conjugation. The xylenes, mesitylene, and pentamethylbenzene were also examined: the halogenation rate of pentamethylbenzene is 4×10^9 that of benzene, per replaceable hydrogen atom.

The chlorination of phenol ethers has been investigated by Bradfield, Jones, and co-workers (J., 1927, 986; 1928, 1006, 3073). These reactions are bimolecular, slightly catalysed by hydrogen chloride, and belong to the class of slow reactions, with P values clustering between 10^{-5} and 10^{-6}. Lauer and Oda (*Ber.*, 1936, **69**, 1061) measured the chlorination rates of aromatic hydrocarbons, including benzene and naphthalene, and concluded (*a*) that although benzene reacts at a much slower rate than naphthalene, there is a lower E value for the reaction, (*b*) that hydrogen chloride retards the chlorination of benzene and has the reverse effect on that of naphthalene, and (*c*) that the action of hydrogen chloride is specific and due to formation of HCl_3. They

accordingly elaborated a theory considered to be in accord with their observations on the absorption spectra of these hydrocarbons. We are unable to confirm these results, and believe that Lauer and Oda failed to realise the importance in chlorination kinetics of errors due to volatility losses of chlorine. With a special technique to reduce that source of error, we, on the contrary, find (*a*) that benzene has a higher heat of activation than naphthalene, and both compounds give *P* values of the same order as the phenol ethers, (*b*) that hydrogen chloride accelerates both reactions, and (*c*) that the effect is not specific, for sulphuric acid is also a catalyst.

The mechanism by which acids in acetic acid solution accelerate the rate of chlorine substitution has not been elucidated. It would appear to be related to the breaking away of the hydrogen ion, for a similar catalysis (to a relatively smaller extent) is found for bromine substitution, but not for chlorine or bromine electrophilic addition to olefinic compounds. Lithium chloride is also a catalyst for both substitutions, and for electrophilic (but not nucleophilic) bromine addition (work to be published). It is known that lithium chloride behaves practically as a strong electrolyte in acetic acid, and its catalytic activity is regarded as a salt effect.

The investigation was extended to the alkylbenzenes, C_6H_5R, where R = Me, Et, Pr$^\beta$, Bu$^\gamma$. The suggestion that alkyl conjugation might operate by an electromeric effect, and consequently be detected by kinetic measurements, was made by Baker and Nathan (J., 1935, 1844). This theory was illustrated by reference to the action of pyridine on members of the series *p*-R·C_6H_4·CH_2Cl, which showed the relative rates 60, 100, 90, 81, and 82 for R = H, Me, Et, Pr$^\beta$, and Bu$^\gamma$ respectively. The relatively small difference in rate between the methyl derivative and the unsubstituted compound made this series unfavourable for the unambiguous detection of the effect under consideration. Hughes, Ingold, and Taher (J., 1930, 949) concluded that unimolecular nucleophilic substitution represented a favourable type of reaction, and measured the hydrolysis of the *p*-alkylbenzhydryl chlorides, C_6H_4R·CHPhCl, in 90% aqueous acetone, finding the relative rates 3·4, 100, 75, 56, and 43 for the same series of substituents, respectively.

Aromatic halogenation is determined by tautomeric electron displacement to carbon atoms at which substitution takes place, followed by the anionisation of the negatively polarised halogen atom of the attacking molecule. In a dissociating solvent such as acetic acid the tendency for side-chain substitution is known to be slight. Such reactions may consequently be regarded as suitable for the comparison of the relative influence of different alkyls, and moreover, the large difference in rate between benzene and toluene, for nitration, indicated the possibility of a well-spaced series. This expectation was justified, as shown by the following relative rates at 24° : I, chlorination in acetic acid; II, bromination in 15% aqueous acetic acid :

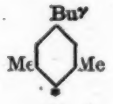
	H.	Me.	Et.	Pr$^\beta$.	Bu$^\gamma$.
I	0·29 *	100	84	51	32
II	—	100	76	44	23

* Owing to the slowness of the benzene reaction this ratio is for 20% aqueous acetic acid at 24°; a second value, in 1% aqueous acetic acid at 35°, is 0·28. The nitration ratio by the competition method is 4·2 (Ingold *et al.*, J., 1931, 1959).

It is possible that the greater divergence in the bromination series may be due to a steric effect, as a result of which bromination is relatively hindered more than chlorination in the *o*-position. In the alkylbenzenes the extent of *o*-substitution (for nitration) decreases from Me ($\frac{1}{2}o : p = 0·80$) to Bu ($\frac{1}{2}o : p = 0·13$) (Ingold, Lapworth, Rothstein, and Ward, J., 1931, 1959; Craig, *J. Amer. Chem. Soc.*, 1930, **52**, 195). This may be related to a variation in the symmetry factor in the mesomeric structures (Bradfield, *Trans. Faraday Soc.*, 1941, 746) or it may be a purely steric effect (Le Fèvre, J., 1938, 980). The values for halogenation are not known; it is clear, however, that the relative fall in rate for *p*-substitution would be less than the fall in total rate, but would still remain considerable. Thus these experiments on the relative rates of halogenation of the alkylbenzenes can be regarded as further evidence of the operation of alkyl conjugation.

A comparison of the relative effects of methyl and *tert.*-butyl was also made in compounds of a different type (total rates of bromination for all available positions in acetic acid at 24·0°) :

100



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As in mesitylene, substitution may take place equally in all three free positions, but in 1 : 3-dimethyl-5-*tert.*-butylbenzene (owing to steric hindrance) almost exclusively in position • ; the comparative rates for the one position become 100 : 39, showing again the greater activity of methyl than of *tert.*-butyl in promoting aromatic substitution.

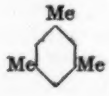
A series of methylbenzenes has also been investigated, giving the following relative rates of halogenation in acetic acid solution :

1

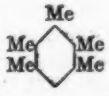
6·3

13·4

$1·25 \times 10^3$



$5·3 \times 10^3$



$2·25 \times 10^4$

The measurement of such great differences in rate between the extreme members of the series was realised by a comparison of the chlorination rates of the first three, and the bromination rates of the last four compounds. The accumulated effect of five methyl groups becomes very considerable. Pentamethylbenzene brominates at about the same rate as anisole, and, per replaceable hydrogen atom, its halogenation rate is 4×10^9 times that of benzene.

Experimental.

The compounds used had the following properties: benzene, b. p. 79·8°/763 mm.; naphthalene, m. p. 80·0°; toluene, b. p. 110·2°/755 mm.; ethylbenzene, b. p. 135·5—136·5°/755 mm.; *iso*propylbenzene, b. p. 150·7—151·0°/756 mm.; *tert.*-butylbenzene, b. p. 165·8°/758 mm.; *o*-xylene, b. p. 142·2—142·5°/750 mm.; *m*-xylene, b. p. 138·5—139·0°/760 mm.; *p*-xylene, b. p. 136·2—136·4°/744 mm.; mesitylene, b. p. 165·0°/760 mm.; pentamethylbenzene, m. p. 53·0—53·5°; 1 : 3-dimethyl-5-*tert.*-butylbenzene, b. p. 201·5—202·3°/752 mm. For the last compound we are indebted to the kindness of Dr. D. V. Nightingale, University of Missouri; fractionation of the specimen yielded fractions with identical rates.

The chlorination technique devised to avoid volatility errors (J., 1939, 1509) has been modified. For the faster reactions, 5 ml. of chlorine solution and 5 ml. of compound solutions are mixed in a brown reaction bottle of only slightly more than 10 c.c. capacity. From this reaction mixture 1 ml. is removed for titration at *ca.* 20% absorption, and a second 1 ml. at *ca.* 40% absorption. A blank is carried out similarly with 5 ml. each of chlorine solution and solvent, 1 ml. portions being titrated when the main titrations are performed. The whole operation is repeated, samples being taken at *ca.* 30% and *ca.* 60% absorption, with corresponding blanks. The % absorptions are calculated, and a curve drawn through the points thus obtained.

Experimental details for M/80-naphthalene + M/80-chlorine in 1% aqueous acetic acid at 24·0° were:

Time (mins.)	5·15	10·35	8·26	18·64
Blank titre (ml.)	2·03	2·01	1·94	1·94
Reaction titre (ml.)	1·45	1·03	1·15	0·66
Absorption, %	28·4	47·9	41·3	67·0

The following are the bimolecular coefficients thus obtained, the k_2 values rising owing to autocatalysis (the corresponding values at M/40 are included for comparison):

Absorption, %	20	30	40	50
k_2 (M/80)	—	6·3	6·7	7·1
k_2 (M/40)	6·0	6·2	6·5	6·7

At 15·3° the values for this reaction were: M/40, $k_2(x = 20) = 4·2$; M/80, $k_2 = 4·1$; E, 7,500 cals. Lauer and Oda gave no experimental details, but summarised: M/30, $k_2(15°) = 3·00$; $(22·5°) = 8·54$; E, 23,450 cals.

For the very slow reactions, one sample only (2 ml.) is removed from the 10 ml. in the reaction bottle, blanks (2 ml.) being run as before. For M/2-benzene + M/20-chlorine in 1% aqueous acetic acid at 34·2°, these results were obtained:

	Time (mins.).	Blank titre (ml.).	Reaction titre (ml.).	$k_2 \times 10^4$.
Expt. I	1610	3·99	3·30	2·38
Expt. II	1475	4·04	3·41	2·34
Expt. III	1512	4·08	3·43	2·31

Hence $k_2(34·2°) = 2·34 \times 10^{-4}$, and as $k_2(24·0°) = 0·89 \times 10^{-4}$, $E = 17{,}000$ cals. Lauer and Oda give for M/30-reactants: $k_2(18°) = 10·5 \times 10^{-4}$, $k_2(30°) = 25·1 \times 10^{-4}$, $E = 12{,}800$ cals. For the effect of hydrogen chloride (amount not specified) they give: $k_2(18°) = 5·7 \times 10^{-4}$. We find for M/2-benzene + M/20-chlorine + 1·31M-hydrogen chloride, $k_2(24·0°) = 4·0 \times 10^{-4}$, showing positive catalysis for benzene as for other compounds on chlorination in acetic acid.

The influence of catalysts is shown as the ratio of catalysed to uncatalysed reactions: M/40-naphthalene + M/40-chlorine + 0·88M-hydrogen chloride, 3·7; +0·51M-sulphuric acid, 4·9; +0·099M-sodium acetate, 1·4; M/10-toluene + M/40-chlorine +0·062M-lithium chloride, 1·57.

The following is a summary of the experimental results for the alkylbenzenes at 24·0°, x being the absorption %, and t the time in mins.:

	M/10-PhR + M/40-Cl_2 in acetic acid.				M/20-PhR + M/20-Br_2 in 85% HOAc + 15% H_2O.			
x.	t (R = Me).	t (R = Et).	t (R = Pr$^\beta$).	t (R = Bu$^\gamma$).	t (R = Me).	t (R = Et).	t (R = Pr$^\beta$).	t (R = Bu$^\gamma$).
10	32·9	39·8	64	106	660	860	1540	2870
15	54·0	63·8	106	167	1130	1480	2570	4970

The values from which the relative rates of the methylbenzenes are calculated are from measurements in acetic acid (99·9%) at 24·0° ($x = 20$), times being in mins.: M/10-toluene + M/40-chlorine, 81·8; *p*-xylene (same concns.), 13·0; *o*-xylene (same concns.), 6·12; M/5-*o*-xylene + M/5-bromine, 283; *m*-xylene (same concns.), 3·02; M/40-*m*-xylene + M/40-bromine, 820; mesitylene (same concns.), 1·95; pentamethylbenzene (same concns.), 0·46.

The relative rates of benzene and toluene are derived from the values in 80% acetic acid + 20% water at 24·0°: M/20-benzene + M/40-chlorine, $t = 240$ mins.; toluene (same concns.), $t = 0·68$ min.

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76. *Catalytic Reduction by Formic Acid under Pressure. Part II. A Comparison of Copper and Nickel as Catalysts.*

By R. Ronald Davies and Herbert H. Hodgson.

Copper, when used as catalyst in conjunction with formic acid, promotes non-nuclear reduction exclusively; *e.g.*, benzaldehyde, benzoic acid, and nitrobenzene are reduced to benzyl alcohol and toluene, to benzene, and to aniline, respectively. Nickel, however, promotes nuclear reduction, *e.g.*, nitrobenzene and phenol are reduced to *cyclo*hexylamine and *cyclo*hexanol, respectively.

SABATIER and MAILHE (*Compt. rend.*, 1910, **151**, 492) found that reduced copper and nickel promoted the decomposition of formic acid into hydrogen and carbon dioxide, and we have adapted this discovery to reductions by formic acid in conjunction with copper or nickel in a sealed tube, and by means of the apparatus described in Part I (this vol., p. 85). *The method has proved of particular service for small-scale hydrogenations*, inasmuch as under sealed-tube conditions the exact amount of hydrogen for any individual hydrogenation may be included in the system as formic acid. It has been found, however, that by the use of copper as catalyst, the reductions of aromatic compounds appear to be exclusively non-nuclear for such typical substances as benzaldehyde, benzoic acid, and nitrobenzene, whereas with nickel as catalyst nuclear hydrogenation is promoted. The results are summarised below. Under identical conditions, benzaldehyde retains its side-chain

Compound hydrogenated.	Catalyst.	Maximum temp. of sealed tube.	Main product.
Benzaldehyde	Copper	200°	Benzyl alcohol and toluene
Benzoic acid	Copper	200	Benzene
Nitrobenzene	Copper	200	Aniline
Nitrobenzene	Nickel	200—220	*cycle*Hexylamine
Phenol	Nickel	200—220	*cyclo*Hexanol

carbon atom and is reduced to benzyl alcohol and toluene, whereas benzoic acid loses carbon dioxide to afford benzene. The method failed with 1 : 8-dinitronaphthalene, and with the dehydration of phenol to diphenyl ether with thoria as catalyst. Sabatier and Mailhe (*loc. cit.*) were probably successful with the latter dehydration because the water would be removed from the reaction zone as formed.

EXPERIMENTAL.

Preparation of Catalysts.—Copper on kieselguhr. Kieselguhr (50 g.) was treated with boiling nitric acid (*d* 1·42), washed with boiling water, and impregnated with 10% aqueous cupric nitrate, followed by immersion in aqueous 2N-sodium hydroxide in amount just sufficient to give final alkalinity to brilliant-yellow paper. The kieselguhr was then removed, washed free from alkali, and dried at 100°. For the subsequent reduction with hydrogen at 300—360°, it was convenient to use the apparatus described in Part I (*loc. cit.*), with the plugs removed, and to pass the gas for an hour. The catalyst was prepared immediately before use.

Nickel catalyst. Kieselguhr (20 g.), pre-treated with nitric acid as above, was shaken for 15 mins. with a 10% aqueous solution of nickel sulphate (200 c.c.), filtered off, and immersed in water (200 c.c.), which was then rendered alkaline to brilliant-yellow paper with sodium carbonate. The kieselguhr was removed, washed free from sulphate and alkali with boiling water, dried at 100°, and reduced immediately before use by heating in a hard-glass tube at 300° for 3 hours in a stream of hydrogen.

Reduction Data.—Copper as catalyst. (i) Benzaldehyde (0·01 g.-mol.), formic acid (0·01 g.-mol.), and the copper–kieselguhr catalyst (1g.) were heated to 200° during 2 hours and maintained at 200° for 1 hour. The product was extracted with ether, washed with water, and dried, and the ether removed; the residual oil (0·92 g.) was redissolved in ether (50 c.c.) and then found to contain benzyl alcohol (*ca.* 56%, estimated by conversion into benzyl acetate), unchanged benzaldehyde (*ca.* 26%, estimated by titration with hydroxylamine hydrochloride; cf. Stillmann and Reed, *Perfume and Essential Oil Record*, 1932, 279), and toluene (*ca.* 18%).

(ii) Benzoic acid (0·01 g.-mol.), formic acid (0·02 g.-mol.), and the copper–kieselguhr catalyst (1 g.) were heated as above, all the aldehyde having then reacted and the product (0·82 g.) being mainly benzene.

(iii) Nitrobenzene (0·01 g.-mol.), formic acid (0·033 g.-mol.), and the copper–kieselguhr catalyst (1 g.) were heated as before. The contents of the tube were washed out with hot 2N-hydrochloric acid, and the solution analysed for aniline both by titration with standard sodium nitrite (Found: 0·0104 g.-mol.) and by diazotisation and coupling with R-salt, the excess of R-salt being estimated by titration with standard benzenediazonium chloride (Found: 0·0101 g.-mol.). The close correspondence between the two results indicated a yield of *ca.* 100% of aniline, with no hydrogenation of the ring. A repeat experiment with double the amount of formic acid gave identical results.

Nickel as catalyst. (i) Nitrobenzene (0·01 g.-mol.), formic acid (0·066 g.-mol.), and the freshly prepared nickel–kieselguhr catalyst (1 g.) were heated as in the foregoing experiments. After extraction of the tube contents with 2N-hydrochloric acid, the filtered extract was made alkaline to brilliant-yellow paper by aqueous sodium hydroxide, and the mixture extracted with ether. The products of two such experiments were combined, the ethereal extracts washed with water and dried with calcium chloride, and the ether removed; the residue of pale yellow oil (1·64 g.) had b. p. 135—137°/760 mm., $n_D^{20°}$ 1·4318 (Found: N, 14·2. Calc. for $C_6H_{13}N$: N, 14·1%). *cyclo*Hexylamine has b. p. 135—138° (Wallach, *Annalen*, 1905, **343**, 46), $n_D^{20°}$ 1·43176.

(ii) Phenol (0·1 g.-mol.), formic acid (0·33 g.-mol.), and the nickel catalyst (3 g.) were heated as above, and the apparatus allowed to cool to room temperature overnight. The contents of the tube were extracted with carbon tetrachloride (100 c.c.), the extract filtered, dried (calcium chloride), and distilled under 765 mm. After the carbon tetrachloride had passed over, the following fractions were collected: up to 155° (2·3 g.), 155—165° (5·2 g.), and 165—190° (3·4 g.). The middle fraction (Found: C, 71·8; H, 11·9. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·0%) was mainly *cyclo*hexanol, and had $d_4^{20°}$ 0·9568, $n_D^{26°}$ 1·4645 (*cyclo*hexanol has b. p. 161°, $d_4^{20°}$ 0·9624, $n_D^{22°}$ 1·4650).

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77. *The Catalytic Dehydrogenation of Alcohols to Aldehydes in the Presence of Air.*

By R. RONALD DAVIES and HERBERT H. HODGSON.

The catalytic dehydrogenation of butyl, dodecyl, and benzyl alcohols mixed with air has been studied in the vapour phase; the optimum yield of aldehyde has been found to depend on a specific air/alcohol ratio for each alcohol. The aldehyde production efficiencies of four varieties of catalyst have been compared. The amount of oxygen consumed is less than that demanded by theory for external oxidation, so dehydrogenation must have occurred.

THE best and probably the most general method for conversion of alcohols into aldehydes is catalytic dehydrogenation, since direct oxidation, *e.g.*, by chromic acid, although fairly successful with aliphatic alcohols of low molecular weight, gives complex mixtures of aldehydes, acids, esters, and acetals with higher alcohols. Such complexity arises even with *n*-butyl alcohol, which is oxidised by chromic acid mainly to *n*-butyl butyrate (cf. Weizmann and Gerrard, J., 1920, **117**, 328). Sabatier and Senderens (*Compt. rend.*, 1903, **136**, 738, 921, 983) found that if alcohols were passed in the vapour phase over reduced copper at 300°, hydrogen was released and the corresponding aldehyde formed. This method was developed by Bouveault (*Bull. Soc. chim.*, 1908, **3**, 50, 119) into a continuous process, the catalyst being formed by reduction at 300° of copper hydroxide precipitated on copper gauze. Weizmann and Gerrard (*loc. cit.*) obtained a theoretical yield of *n*-butaldehyde from *n*-butyl alcohol by the Bouveault procedure, and Moureu and Mignonac (*Compt. rend.*, 1920, **170**, 258) minimised the reversible reduction back to alcohol by the liberated hydrogen by using a copper–silver catalyst [cf. also Aleksandrova, *J. Appl. Chem. U.S.S.R.*, 1937, **10**, 105 (*Chem. Abs.*, 1937, 4206)].

The present investigation was designed to ascertain the general applicability of the above process modified by admixture of the alcohol with air; butyl, dodecyl, and benzyl alcohols were selected for the purpose, and the efficiencies of four varieties of catalyst have been compared. The experimental data indicated that dehydrogenation was best effected by a copper–silver catalyst on pumice and within a temperature range of 300—350°. A definite air/alcohol ratio appears to be specific for a maximum yield of aldehyde, the optimum amount of air being in all cases well below the theoretical value for oxidation by the oxygen; *e.g.*, for *n*-butyl alcohol the amount of oxygen consumed was only 13% of the theoretical. Further, the aldehyde produced was comparatively pure, and the main by-product (only present in small quantities) was the corresponding carboxylic acid. This ultimate oxidation to acid was less pronounced with the saturated aliphatic alcohols than with benzyl alcohol. When too much oxygen was used (*i.e.*, excess over the particular amount which produced the optimum yield of aldehyde), oxidation proceeded to the carboxylic acid even though the total oxygen consumed from the air was still less than theory demanded for external oxidation. It would appear, therefore, that the mechanism is twofold, *viz.*, catalytic oxidation of the alcohol by the air alongside catalytic dehydrogenation of the alcohol to aldehyde and hydrogen. It is suggested that one function of the atmospheric oxygen is to remove hydrogen adsorbed at the surface of the catalyst.

EXPERIMENTAL.

Apparatus.—A 250-c.c. bolt-head flask, heated in an oil-bath, was fitted with a bung having 3 apertures through which passed an air inlet connected with a flow-meter (capable of measuring air velocities of 0—3000 c.c./min.), a dropping funnel, and a connection to a copper tube (1 m. long and 2 cm. in diam.) containing the catalyst, through which the reacting gases passed, *via* a glass tube, to a condenser attached to a distillation flask which could be connected directly to a vacuum pump if required. The copper tube was provided with thermometers at each end.

Preparation of the Four Catalysts used for Comparison Purposes.—(a) *Copper on kieselguhr.* The kieselguhr (50 g.) was prepared and impregnated as described in the preceding paper.

(b) *Copper–silver on kieselguhr.* The copper–kieselguhr above was immersed in 10 times its weight of 10% ammoniacal silver nitrate, removed, washed free from ammonia with water, and dried in a stream of hydrogen.

(c) *Copper–silver on pumice.* The procedure was as for (a) with pumice (lumps of *ca.* 0·2 cm. diam.) instead of kieselguhr, and silver was deposited as for (b).

(d) *Silver on copper gauze.* The copper gauze (100 mesh) was cleaned by 10 mins.' immersion in 10% ammoniacal silver nitrate, washed, and dried as under (b).

Method of Working.—The oil-bath for heating the flask was set at a temperature 20° higher than the b. p. of the alcohol to be hydrogenated, which was added from the graduated dropping funnel at a predetermined rate, the air current being also regulated by the flowmeter, and the catalyst maintained at a given temperature. When the reaction had commenced in the catalyst tube, very little additional heat was required, but regulation of the heating to secure the fixed temperature was easily effected by gas burners.

Dehydration of Butyl Alcohol.—The results are in Table I, fuller details of expts. 11, 18, and 19, which were conducted with 200 g. of *n*-butyl alcohol, being given in Table II.

For butyl alcohol at atmospheric pressure and with a flow ratio of 1000 c.c. of air to 10 c.c. of alcohol per min., there is little to choose between the copper–silver on pumice and the silver on copper gauze catalysts, whereas the copper–silver kieselguhr catalyst gave poor results, a circumstance attributed to alteration of gas ratio by partial choking. Copper gauze alone gave reasonable yields of aldehyde, although they were slightly contaminated with butyric acid. The copper–silver catalysts which had been deactivated by prolonged exposure to atmospheric conditions were readily re-activated by renewed treatment with ammoniacal silver nitrate.

Optimum conditions for aldehyde formation at atmospheric pressure. These are indicated by expts. 11, 18, and 19, where the products contained only traces of *n*-butyric acid, *viz.*, by the use of a copper–silver catalyst on pumice at 350° with an air/alcohol ratio of 500/5 c.c. per min. Increase in the proportion of air or replacement of the copper–silver catalyst by copper resulted in an increase in the amount of *n*-butyric acid produced, whereas decrease in the proportion of air decreased the conversion.

Method of analysis (also employed for the dodecyl and *n*-butyl alcohol experiments). The total condensate from each experiment was dissolved in ether, separated from water, and dried over sodium sulphate, the ether removed, and the residual oil weighed. The oil (20 g.) was dissolved in ether (100 c.c.) and shaken three times with 10% aqueous sodium bisulphite (3 × 100 c.c.), the ethereal part being used for the estimations. (*a*) In one half, acid was determined by direct titration with 0·2N-alcoholic potassium hydroxide (phenolphthalein indicator) and (*b*) ester by adding to the titrated solution 20 c.c. of 0·2N-alcoholic potassium hydroxide, boiling the mixture under reflux for 2 hours, and subsequently back-titrating it with 0·2N-sulphuric acid, the amount of ester being calculated as *n*-butyl butyrate. In the other half, (*c*) unchanged alcohol was determined by evaporating the solution at 50°, and estimating the alcohol content in the residue by acetylation, followed by determination of the saponification value, allowance being made for the amount of ester present. (*d*) The above bisulphite solution was heated with sulphuric acid for 1 hour under reflux, the liberated aldehyde extracted by ether, and estimated by Stillmann and Reed's method (*Perfume and Essential Oil Record*, 1932, 279).

Identification of the aldehyde formed. The oil (470 g.) from expts. 11, 18, and 19, remaining after analysis, was shaken

TABLE I.

Effect of catalyst, air/alcohol ratio, and temperature on the yield of n-*butaldehyde.*

Expt.	Air vel., c.c./min.	Alcohol vel., c.c./min.	Catalyst.	Temp.	Conversion, %.	Yield after allowance for recovery of alcohol, %.
1	500	5	(a)	300°	63	86
2	1000	5	,,	300	68	83·5
3	2000	10	,,	300	73	83
4	2000	10	,,	350	69	72
5	2000	10	(b)	300	64	86
6	500	5	,,	250	52	87
7	1000	5	,,	350	86	82
8	1000	5	(c)	300	69	89
9	1000	5	,,	350	87	88
10	1000	5	,,	400	82	84
11	500	5	,,	350	89	96
12	500	5	Cu	350	73	87
13	1000	5	,,	350	81	84
14	500	5	,,	300	67	85·6
15	500	5	(d)	350	88	92
16	1000	5	,,	350	89	86
17	500	5	,,	300	72	93
18	500	5	(c)	350	90	94 †
19	500	5	,,	350	88	97 †

* Choking was troublesome in all experiments with kieselguhr.
† Expt. 11 was repeated with the same catalyst revivified.

TABLE II.

Expt.	Weight of oil, g.	Aldehyde, g.	Aldehyde, %.	Alcohol recovered, g.	Alcohol recovered, %.	Conversion, %.	Yields, %. Aldehyde.	Ester.	Acid.
11	192	166	86·5	22	11·5	89	96	0·5	—
18	189	164·5	87·0	20	10·6	90	94	1·2	0·2
19	194	166	85·5	24	12·4	88	97	0·3	0·6

with 3 portions of 10% sodium bisulphite solution (total 500 c.c.). The combined bisulphite liquors were extracted twice with ether (600 c.c.), the aqueous solution hydrolysed with hydrochloric acid, the aldehyde extracted therefrom with ether, and the ether evaporated. This left 394 g. of oil, which, after addition of sodium carbonate (2 g.), was fractionated with a 2′ column packed with ¼″ Lessing rings for the lower 20″; 3 fractions were coolected at 764 mm., *viz.*, up to 70° (30 g.), b. p. 70—73° (326 g.), and b. p. 78—90° (20 g.). The middle fraction had $n_D^{20°}$ 1·3844, $d_4^{20°}$ 0·8152, and was *n*-butaldehyde ($n_D^{20°}$ 1·3843, $d_4^{20°}$ 0·817, b. p. 74°/760 mm.).

Dehydrogenation of Dodecyl Alcohol (*setting point*, 22°).—The results are in Table III, 200 g. of the alcohol and catalyst

TABLE III.

Expt.	Air vel., c.c./min.	Alcohol vel., c.c./min.	Temp.	Pressure, mm.	Alcohol consumed, %.	Weight of product, g.	Aldehyde formed, %.	Acid, %.
1	500	5	350°	760	93	193	79	12·2
2	500	5	350	100	91	195	81	8·3
3	500	5	350	20	94	192	76	16·3
4	250	5	350	100	86	194	88	—
5	250	5	250	100	63	198	82	—
6	200	5	300	100	88·5	191	85	2·1

(c) being used. The optimum conditions, which afforded a yield of 88%, were therefore: alcohol velocity, 5 c.c./min.; air velocity, 250 c.c./min.; temperature, 300—350°; pressure, 100 mm. The increased proportion of lauric acid, compared with that of *n*-butyric acid in the dehydrogenation of *n*-butyl alcohol, is noteworthy, and the reaction appeared to be less exothermic.

Dehydrogenation of Benzyl Alcohol.—200 G. were used, with catalyst (c) and atmospheric pressure, since no advantage accrued from working at lower pressures. The results (below) show that the optimum conditions (76·5% yield) are a

TABLE IV.

Expt.	Air vel., c.c./min.	Alcohol vel., c.c./min.	Temp.	Alcohol consumed, %.	Weight of product, g.	Aldehyde formed, %.	Acid, %.
1	500	5	300°	63	200	61·5	16·0
2	750	5	300	77	197	76·6	12·2
3	1000	5	300	71	198	70·6	17·0
4	750	5	350	76	196	76·0	10·1

ratio of 750 c.c. air/5 c.c. alcohol per min. at 300—350°. The yields of aldehydes in all cases are below those for the aliphatic alcohols (above), and an appreciable amount of benzoic acid was formed, the reaction being less exothermic than for *n*-butyl alcohol.

TECHNICAL COLLEGE, HUDDERSFIELD.

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78. N-*Nitrosoaceto*-1-*naphthalide.*

By Herbert H. Hodgson and Ewart Marsden.

N-*Nitrosoaceto*-1-*naphthalide* is formed when a solution of aceto-1-naphthalide in glacial acetic acid is added to nitrosylsulphuric acid. Its reactions are similar to those of a diazonium compound in mineral acid (*e.g.*, Sandmeyer reaction) and of a diazo-compound (*e.g.*, coupling) in neutral, weak acid, and alkaline solution.

Grieve and Hey (J., 1935, 689) failed to obtain *N*-nitrosoaceto-1-naphthalide by passing nitrous fumes into a solution of aceto-1-naphthalide in glacial acetic acid. We also failed, using an ethyl-alcoholic solution. Complete and rapid formation of N-*nitrosoaceto*-1-*naphthalide*, however, occurred when aceto-1-naphthalide was treated by the Hodgson–Walker method of diazotisation (J., 1933, 1620). Crystals were actually obtained, but with difficulty; nevertheless, the tarry product gave 1-chloronaphthalene with the Sandmeyer reagent, a mixture of 2- and 4-nitro-1-naphthols with ethyl alcohol, and naphthalene together with the above nitronaphthols with copper powder. In these reactions, the nitroso-compound must have been hydrolysed into the diazonium salt prior to decomposition. Moreover, *N*-nitrosoaceto-1-naphthalide coupled rapidly with β-naphthol in alkaline solution, readily with α- and β-naphthylamine in acetic acid, and more slowly with α-naphthol, α-naphthylamine, and H-acid in neutral environment. These couplings indicate that hydrolysis and consequent formation of a reactive diazo-compound (cf. Bamberger and Müller, *Annalen*, 1900, **313**, 126) precede coupling.

α-Naphthylamine itself is stated to be incapable of diazotisation by nitrosylsulphuric acid (E.P. 355,970; D.R.-P. 519,729), but is nitrosated in the *p*-position to the amino-group. Acylation of the amino-group consequently inhibits this *p*-nitrosation, and, in effect, promotes diazotisation.

Experimental.

Nitrosation of Aceto-1-*naphthalide.*—A solution of aceto-1-naphthalide (18·5 g.) in glacial acetic acid (185 c.c.) was added during 1 hour to an ice-cooled solution of sodium nitrite (7·7 g.) in sulphuric acid (60 c.c., *d* 1·84); a vigorous reaction occurred and the temperature had to be maintained below 20°. After 30 minutes, the mixture was poured into ice-water (2 l.); the yellowish tar which slowly settled was separated from the aqueous layer, washed with water (200 c.c.), dried, and washed with carbon tetrachloride and carbon disulphide, in which it was insoluble. On keeping at −20°, yellow needles (0·7 g.) of N-*nitrosoaceto*-1-*naphthalide* formed, m. p. 8—10°, which were rapidly pressed between filter-paper (Found: N, 13·0. $C_{12}H_{10}O_2N_2$ requires N, 13·1%). They were very unstable and changed into a yellow oil which decomposed smoothly and rapidly at room temperature with evolution of nitrogen. That the tar consisted essentially of *N*-nitrosoaceto-1-naphthalide was established by the following experiments.

(*a*) When the tar (from 18·5 g. of aceto-1-naphthalide) was added to a solution of cuprous chloride (20 g.) in hydrochloric acid (50 c.c., *d* 1·16), a violent reaction began. After 30 minutes, the mixture was steam-distilled, α-chloronaphthalene (10 g.; yield, 61·8%) passing over.

(*b*) Another batch of tar, prepared as above, was mixed with ethyl alcohol (100 c.c.), kept overnight, heated to 80° on the water-bath, and then steam-distilled; a small amount of 2-nitro-1-naphthol passed over. The residual liquor was filtered hot; on cooling, it deposited a mixture of 2- and 4-nitro-1-naphthols (10·02 g.; 53·7% yield). These were separated by means of the difference in solubility of their potassium salts in water (Hodgson and Kilner, J., 1924, **125**, 808), 45% of 2-nitro-1-naphthol and 54% of 4-nitro-1-naphthol being obtained. The addition of copper powder to the alcoholic mixture was without effect on the products of the reaction.

(*c*) The initially prepared solution of *N*-nitrosoaceto-1-naphthalide (above) was mixed with copper powder (6·3 g.) at 20—30° and kept overnight. On steam-distillation, naphthalene (0·9 g.; 8% yield) was obtained, together with 2- and 4-nitro-1-naphthols (48% yield) and a tar (0·6 g.). The nitronaphthols were present in the proportion 52% of the 1 : 2- and 48% of the 1 : 4-isomeride.

(*d*) The tar, prepared as above, was stirred into a faintly alkaline solution of β-naphthol (14·3 g.) in aqueous sodium hydroxide, to which sodium carbonate was subsequently added. After keeping overnight, 1-1′-naphthaleneazo-2-naphthol was precipitated (23·0 g.; 78% yield).

(*e*) The Gomberg reaction did not occur when the tar was dissolved in benzene and kept overnight; nitronaphthols were formed, but no 1-phenylnaphthalene was observed.

(*f*) Coupling occurred in the following experiments, immediately in (i) and (iv), slowly in (ii) and (iii). (i) The *N*-nitrosoaceto-1-naphthalide solution (188 c.c.) prepared from 18·5 g. of aceto-1-naphthalide was divided into two equal parts, each of which was further diluted with acetic acid and then treated with sodium acetate until it gave no blue colour with Congo-red paper. The two solutions were then added gradually at 0—5° to solutions of α- and β-naphthylamine (5 g.) in glacial acetic acid (40 c.c.) diluted with water (100 c.c.) in which sodium acetate had been dissolved. (ii) α-Naphthol (5 g.) was dissolved in just sufficient sodium carbonate (2N), the solution faintly acidified with hydrochloric acid, the excess of acid neutralised with calcium carbonate, and ethyl alcohol (150 c.c.) added. The tar (prepared from 9·25 g. of aceto-1-naphthalide and made neutral by calcium carbonate) was stirred into the above mixture. (iii) A solution of α-naphthylamine (5 g.) in ethyl alcohol (100 c.c.) was diluted with ice and water to 250 c.c., calcium carbonate (20 g.) stirred into the suspension, and tar, prepared and neutralised as above, stirred into the mixture. (iv) A solution of H-acid (5 g.) in just sufficient sodium carbonate (2N) was diluted with ice and water to 250 c.c. and faintly acidified with dilute hydrochloric acid, calcium carbonate added in excess, followed by neutral tar prepared as above.

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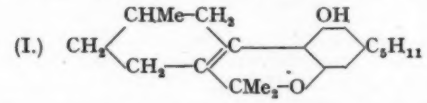
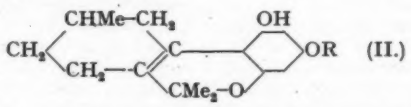
79. *Cannabis Indica. Part XII. Some Analogues and a Water-soluble Derivative of Tetrahydrocannabinol.*

By F. Bergel, A. L. Morrison, H. Rinderknecht, A. R. Todd, A. D. Macdonald, and G. Woolfe.

Four analogues of tetrahydrocannabinol (I) in which the *n*-amyl group is replaced by *n*-alkoxy-groups have been prepared. Of these, only (II; R = *n*-C_6H_{13}) appeared to show hashish activity in rabbits. Disodium tetrahydrocannabinyl phosphate, a water-soluble material, has also been prepared. It showed no activity when tested on rabbits by the Gayer method.

In previous papers (Russell, Todd, Wilkinson, Macdonald, and Woolfe, J., 1941, 169, 826) we described the preparation of a variety of analogues of tetrahydrocannabinol (I), using the general synthetic method of Ghosh, Todd, and Wilkinson (J., 1940, 1121), and reported the results of their pharmacological examination for hashish activity, using the Gayer test on rabbits. Among the synthetic analogues those in which the size of the alkyl substituent in the aromatic ring varied from methyl to octyl proved perhaps the most interesting from the standpoint of the relation between hashish activity and chemical constitution, activity in the *n*-alkyl series rising to a maximum in the hexyl and heptyl analogues, both of which were considerably more potent than (I). The same series of analogues was also prepared by Adams, Loewe, Zelinek, and Wolff (*J. Amer. Chem. Soc.*, 1941, **63**, 1971) and examined pharmacologically by the dog ataxia method; by this test the *n*-hexyl analogue clearly represented the peak of activity. Differences of this type in the relative potencies of various compounds reported by the American workers and ourselves are almost certainly due to the different biological tests employed. The striking gradation of activity observed in this series of compounds caused us to include in our investigations an examination of analogues of type (II) in which the *n*-amyl group of tetrahydrocannabinol (I) is replaced by *n*-alkoxy-groups of varying size. We prepared in all four compounds of type (II) in which R = *n*-C_4H_9, -C_5H_{11}, -C_6H_{13}, -C_7H_{15}, and we wish to place our results on record. The compounds described were prepared by condensation of 4'' : 6''-dihydroxy-2 : 2 : 5'-trimethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran (Ghosh, Todd, and Wilkinson, *loc. cit.*) with the appropriate alkyl bromide in presence of alcoholic sodium ethoxide. Under the conditions employed, only the 4''-hydroxyl was alkylated, since the products, viscous amber-coloured oils, gave an intense blue coloration with 2 : 6-dichloroquinonechloroimide, indicating the presence in them of a phenolic hydroxyl group, the *p*-position to which was unsubstituted. When tested on rabbits by the Gayer method, *6''-hydroxy-4''-n-hexyloxy-2 : 2 : 5'-trimethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran* (II; R = *n*-C_6H_{13}) appeared to show feeble activity in doses between 10 and 20 mg./kg., but none of the other substances showed any activity in doses up to 20 mg./kg.





In view of possible clinical application of synthetic hashish-active substances, it seemed of interest to prepare a water-soluble derivative of tetrahydrocannabinol. To this end, following a model experiment on the readily accessible 6''-hydroxy-2 : 2 : 5' : 4''-tetramethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran (Ghosh, Todd, and Wilkinson, *loc. cit.*), tetrahydrocannabinol (I) was brought into reaction with phosphoryl chloride in pyridine solution, and the resulting O-*dichlorophosphoryltetrahydrocannabinol* converted into the readily soluble disodium tetrahydrocannabinyl phosphate. The product showed no apparent hashish activity in rabbits (Gayer test) in a dose of 20 mg./kg. This finding was unexpected, since it had already been observed that the acetate of tetrahydrocannabinol is active in the Gayer test, although it is slower in action than tetrahydrocannabinol itself (Leaf, Todd, and Wilkinson, J., 1942, 185). The only reasonable explanation would appear to be a greater resistance of the phosphate to hydrolysis.

Experimental.

6''-Hydroxy-4''-n-hexyloxy-2 : 2 : 5'-trimethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran (II; R = *n*-C_6H_{13}).—To alcoholic sodium ethoxide (0·23 g. of sodium in 22 c.c. of absolute alcohol), 4'' : 6''-dihydroxy-2 : 2 : 5'-trimethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran (II; R = H) (2·6 g.) and *n*-hexyl bromide (2·15 g.) were added, and the mixture heated in a sealed tube in a boiling water-bath for 15 hours. The liquid was filtered and evaporated, and the residue taken up in ether, washed with dilute hydrochloric acid, sodium bicarbonate solution and water, and dried over anhydrous sodium sulphate. After removal of the ether the product (2·2 g.) distilled at 205—209° (bath temp.)/0·2 mm. as a viscous amber-coloured oil (Found: C, 76·9; H, 9·5. $C_{22}H_{32}O_3$ requires C, 76·8; H, 9·3%).

The following compounds were prepared in similar fashion: *6''-Hydroxy-4''-n-butoxy-2 : 2 : 5'-trimethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran* (II; R = *n*-C_4H_9); distilled at 185—189° (bath temp.)/0·01 mm. (Found: C, 75·9; H, 9·2. $C_{20}H_{28}O_3$ requires C, 76·0; H, 8·9%). *6''-Hydroxy-4''-n-amyloxy-2 : 2 : 5'-trimethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran* (II; R = *n*-C_5H_{11}); distilled at 205—210° (bath temp.)/0·1 mm. (Found: C, 77·0; H, 9·6. $C_{21}H_{30}O_3$ requires C, 76·4; H, 9·1%). *6''-Hydroxy-4''-n-heptyloxy-2 : 2 : 5'-trimethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran* (II; R = *n*-C_7H_{15}); distilled at 210—215° (bath temp.)/0·15 mm. (Found: C, 77·0; H, 9·5. $C_{23}H_{34}O_3$ requires C, 77·1; H, 9·5%).

6''-O-Dichlorophosphoryl-2 : 2 : 5' : 4''-tetramethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran.—To 6''-hydroxy-2 : 2 : 5' : 4''-tetramethyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyran (0·7 g.), dissolved in dry pyridine (2·5 c.c.) and cooled in ice, phosphoryl chloride (0·6 g.) was added. After several hours the mixture was refluxed for 30 mins., cooled, and extracted twice with dry benzene. The extract was evaporated under reduced pressure to remove solvents, and again after addition of more

dry benzene. The residue was distilled, giving a colourless oil (0·6 g.) at 170° (bath temp.)/0·15 mm. (Found : C, 53·6, 55·0; H, 6·2, 6·3; Cl, 18·3. $C_{17}H_{21}O_5Cl_2P$ requires C, 54·3; H, 5·6; Cl, 18·9%).

The *dichlorophosphoryl* derivative (0·55 g.) in ethereal solution was shaken with water for 3 hours; titration then showed that 99% had been converted into the corresponding acid. The ethereal solution was washed with water, dried, and evaporated, and the viscous residue treated with alcoholic sodium hydroxide (2 mols.). The corresponding *disodium phosphate* was obtained as a white hygroscopic powder by precipitation with dry ether (Found : C, 49·0; H, 6·2. $C_{17}H_{21}O_5PNa_2.2H_2O$ requires C, 48·8; H, 6·0%).

O-*Dichlorophosphoryltetrahydrocannabinol.*—Prepared in similar fashion from tetrahydrocannabinol (I), the *product* was a colourless oil distilling at 185° (bath temp.)/0·1 mm. (Found : C, 57·5; H, 6·9; Cl, 16·5. $C_{21}H_{29}O_5Cl_2P$ requires C, 58·5; H, 6·7; Cl, 16·5%). The corresponding disodium phosphate, a white hygroscopic powder, was prepared by the method described above; in this case hydrolysis of the dichlorophosphoryl derivative was slower. After 3 days' standing in the refrigerator 50% of the phosphoryl compound was hydrolysed. A further 3 hours of shaking with fresh water were necessary for completion of the hydrolysis.

Tetrahydrocannabinyl Phosphate.—The above sodium salt was dissolved in water, the solution acidified with hydrochloric acid, and the *phosphate* extracted with ether. Removal of the ether left a viscous oil, which was dried in a vacuum at 50° (Found : C, 64·0; H, 7·9. $C_{21}H_{31}O_5P$ requires C, 64·0; H, 7·9%).

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